International Workshop
on Corrosion Control
for Marine Structures and Pipelines

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Table of Contents

Inspection of Pipelines Based on Reliability
Juan Matias Acevedo, Instituto Mexicano del Petroleo

Plenary Presentations

Deep Water Corrosion Control Design
Jim Britton, Deepwater Corrosion Services, Inc.

The Coming of Age of Titanium for Application to Marine and Offshore
Oil & Gas Systems
James S. Grauman, TIMET - Henderson Technical Laboratory
John Barber, TIMET - Corporate Development Group

Composite Material Offshore Corrosion Solutions
Jerry G. Williams, Composites Engineering and Applications Center

Special Topic Presentation

Economic Considerations in Material Selection for Offshore Oil & Gas
Production Applications
Derek Pattle, Wyman-Gordon Co.

Theme Papers

Overview on Materials Challenges
James F. Jenkins, Nickel Development Institute

Metallic Coatings for Corrosion Control of Marine Structures
Dale T. Peters, Copper Development Association Inc.
Harold T. Michels, Copper Development Association Inc.
Carol A. Powell, Nickel Development Institute

Coatings: Organic
Richard D. Granata, Florida Atlantic University

Cathodic Protection of Offshore Structures and Pipelines - Historical Development, Present Knowledge, and Future Challenges
William H. Hartt, Florida Atlantic University

High Strength Fasteners for Seawater Immersion Service
D.M. Aylor, Naval Surface Warfare Center, Carderock Division
C.A. Bowles, Naval Surface Warfare Center, Carderock Division
R.L. Tregoning, Naval Surface Warfare Center, Carderock Division
M.A. Gaudett, Naval Surface Warfare Center, Carderock Division

Structural Testing of Corroded Offshore Tubular Members
James M. Ricles, Lehigh University
Michael Hebor, Lehigh University
Duncan Paterson, Lehigh University

Corrosion and Materials Challenges for Deep Water Oil and Gas Production
R.D. Kane, InterCorr International, Inc.
M.S. Cayard, InterCorr International, Inc.
H.R. Hanson, InterCorr International, Inc.

Corrosion Protection of Ballast and Cargo Tanks of Crude Oil Tankers
R.T. Huang, Chevron Shipping Company

Working Group Reports

Corrosion Protection of Deepwater Subsea Structures and Pipes
R.T. Hill, Aker Maritime, Inc.
M. Karayaka, Aker Maritime, Inc.

Corrosion Control for Ship Structures
Phil Rynn, American Bureau of Shipping
William Hanzalek, American Bureau of Shipping
John Kelly, Naval Surface Warfare Center, Carderock Division
Akzo Nobel, Naval Surface Warfare Center, Carderock Division

Christine Bowles, Naval Surface Warfare Center, Carderock Division

Corrosion in Floating Structures
Bard Espelid, Det Norske Veritas
Einar Tore Moe, Det Norske Veritas

Corrosion Protection of Fixed Offshore Structures
R.D. Holdsworth, Risk, Reliability and Safety Engineering
D.W. Townley, Chevron Research and Technology Company

Corrosion in Pipelines
R.W. Revie, CANMET Materials Technology Laboratory
R.D. Huriaux, Office of Pipeline Safety

Materials Status and Developments for Oil and Gas Industry Offshore Topside
Torfinn Havn, Aker Maritime, Stavanger
Juri Kolts, Conoco, Inc.
Mamdouh Salama, Conoco, Inc.
Robert N. Tuttle, Corupdate, Inc.

Corrosion Control in Ports and Harbors
Martin Eskijian, Marine Facilities Division
Tom Spencer, Blaylock Engineering Group
Dan Polly, NFESC
Ben Gerwick, Ben Gerwick, Inc.
Ron Heffron, Han-Padron Associates

Workshop Critiques
William H. Hartt, professor and Director
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EXECUTIVE SUMMARY

The practices of marine corrosion control for offshore structures, pipelines, risers, production machinery, and ship structures is in continual change due to new corrosive environments, increasing structural design requirements, new tools to assess damage, new concepts of protection, and the ever-increasing use of advanced materials. Advanced materials here include titanium alloys, copper and nickel-base alloys, fiber-reinforced plastics, other composite materials, and new coating materials. The marine industry is very familiar with corrosion in severe environments, and has developed the necessary technologies to control corrosion for economical production of petroleum and for acceptable ship performance. Today, the most stringent corrosion problem is the increasing depth of underwater petroleum production. These new depths will require new materials, more corrosion data, and new modifications of the present corrosion protection systems. At this time, deep-water subsea structures and production systems are operating at xxxx meters.

The corrosive environment in internal Pipelines and container and ballast tanks also remains a continuing technological challenge. Advances in corrosion protection result from new techniques for cathodic protection. New coatings, and the introduction of new materials, all of which are required to extend component life in severe environments.

This "Corrosion Control for Marine Structures and Pipeline " Workshop has been designed to define current status of corrosion protection, to identify the technical and non-technical barriers that hinder a fuller utilization of advanced methods for mitigating corrosion, and to identify research and development projects that would advance corrosion control technologies. This book presents both the state-of-the-art papers and the discussion papers resulting from the workshop. Specific recommendations are made for both research and development needs. Focusing on the topics of marine corrosion control, the authors and participants, all experts in marine corrosion, have made the book a benchmark statement of marine corrosion control.

Many of the research and development studies recommended are progressive in nature, but improving the existing technologies. Improving the selection of materials and the corrosion protection practices can advance the design and use of internal pipeline, ballast and container tanks, and ships. Coating research on both the material and deposition process offers potentially significant improvements, and will allow cost-effective structural materials to serve well in the more aggressive environments.

Revolutionary research and development efforts are more timely now that deepwater subsea production requires the use of high specific strength materials in significantly different corrosive environment. Machinery must also provide longer service life, and inspection of these deepwater systems can be difficult. New materials, advanced coatings and efficient cathodic protection systems must be developed, validated by industry and implemented.

The book contains invited information papers for state-of-the-art information in the sections of Keynote lectures, Plenary lectures, and theme papers. The white (discussion) papers were prepared by each discussion group leader and were debated and modified to express the opinions and recommendations of the group. These recommendations have been extracted form the text, categorized by various disciplines and listed in the beginning portion of the book. The editors also summarized and prioritized the

recommendations to identify the most needed and promising research and development opportunities.

Introduction

Corrosion of marine structures, pipelines, and harbor structures, represents a significant loss to the operational cost, productivity for the older structures. An assessment of the effectiveness of using newer materials and repair technologies plays a serious role in the investment decisions concerning life extension, through repair and modification, of older marine structures and pipelines. Also, such an assessment, including the best advanced corrosion protection and corrosion damage repair technologies, would help prioritize investment in new corrosion-related research. The best forum for an assessment like that described above is a dynamic workshop.

In addition, corrosion data acquisition is very expensive and the various offshore operators utilize a variety of primary corrosion protection techniques, a corrosion workshop is the most appropriate forum for: 1) disseminating and transferring information, 2) learning about new technologies and materials, 3) assessing future needs, and 4) defining the best opportunities for research.

New technologies for remotely sensing the corrosion damage of offshore processing equipment, structures and pipeline are important for reducing the number of personnel working offshore and thus reducing personal injury liability. Implementation of advanced computer systems will allow data acquisition from shore, and will thus increase the safety of personnel responsible for maintenance of marine structures and pipelines.

New coating materials, as well as environmentally acceptable application and removal techniques, are now currently available, and operators must follow advances in these coating developments. New understanding of corrosion mechanisms associated with corrosion damage of marine structures and pipelines is also evolving, and offers new approaches to alleviate future damage, for example, the synergistic effects of cathodic protection and hydrogen assisted corrosion fatigue behavior are now better understood. These results suggest modifications in some cathodic protection practices.

It was with these ideas in mind that the International Workshop on Corrosion Control for Marine Structures and Pipelines was organized. An organizing committee consisting of recognized experts from around the world was established in late 1997 to put together a program that will:

a. discuss the effectiveness of various methods of corrosion protection.
b. identify both the technical and non-technical hindrance to the application of new corrosion protection methods.
c. identify corrosion tests required to establish acceptability for designers and maintenance and corrosion", engineers.
d. identify the research activities that can significantly improve corrosion resistance, and thus deserve support.
e. provide an international forum, attracting participants from all aspects of material production and utilization (corporate leadership, designers, maintenance engineers, inspectors, and corrosion engineers).
f. promote the use of cost-effective advanced corrosion protection methods in marine structures and pipelines
g. produce an archival record (planned to be a hardbound book) which thoroughly describes both the current corrosion protection practices and the opportunities for fuller utilization.

A careful balance of: 1) presentations on current status of corrosion protection methods at the research and production levels, 2) position white papers from working group discussions on specific corrosion related issues, and 3) identification of the educational, research, and development needs regarding advancement in corrosion protection technologies, will be established.

Workshop Overview

The Workshop took place in the San Luis Resort and Conference Center, Galveston, Texas between February 9 and 11, 1999, with a total of around 150 participants. The meeting opened with a series of short supporting remarks by several government and industry leaders. They all emphasized the importance and increasing needs for advanced corrosion control in marine structures and pipelines, and encouraged the participants to actively contribute to the workshop. Following the supporting remarks, several key industrial experts were invited to speak on topics related to fundamentals of corrosion, corrosion inspection, environmental concerns, and risk and reliability analysis. The program followed with seven theme presentations that provided the attendees with current state-of-the-art information corrosion monitoring and protection, materials challenges. The topics are:

- Overview on materials challenges
- Coatings: Metallic
- Coatings: Organic
- Cathodic Protection
- Fastener Corrosion
- Corrosion Monitoring: Testing and Inspection
- Pipeline Corrosion Monitoring

Several other topical/plenary presentations were also made during the Workshop. Concrete in the Marine Environment, Selection Criteria for Materials in the Offshore Environment, Deep Water Corrosion, The Coming of Age of Titanium in Marine Applications, and Composites in Marine Applications. The manuscripts of these presentations are included in this volume.

One of the major goals of the workshop was to promote interchange of technical information among producers, designers, engineers, fabricators, inspectors, and users of marine materials. Eight working group sessions were planned to review and revise position papers (prepared by groups of experts prior to the workshop and distributed to all participants at registration). The Working groups focused on corrosion in:

- Subsea Structure and Pipes
- Ship Structures
- Floating Structures
- Fixed Structures
- Pipelines
- Harbors
- Topside Processing Equipment

The activities of each working group were based on the presentation of a white paper which identified the research and development needs of materials with unique properties required for marine applications. The position papers also discussed opportunities and important ongoing projects, and barriers to the progress in corrosion protection. In marine structures and pipelines. During the working group period, the participants were encouraged to visit more than one session to maximize their contributions to the different groups. For the final session of the working groups, the participants were charged to prepare lists of prioritized action items for the final workshop assembly.

On the morning of February 7, 1997, the working group leaders came back to report to the full group on their conclusions and recommendations. These important discussions are included in this volume. At the conclusion of the workshop, Dr. Bill Hartt, a world renowned specialist in corrosion, provided critique of the workshop. He was positive and upbeat, and found the workshop extremely worthwhile for information exchange on future trends in corrosion research and development in marine and pipeline industries.

Acknowledgment

Prioritized Research and Development Recommendations for Corrosion Control for Marine Structures and Pipelines

RECOMMENDATIONS

Recommendations from the working groups have been categorized by topical areas to more clearly analyze and formulate a meaningful response. The categories are materials, design, protection, inspection, reliability, corrosion science, and education and training. The supporting descriptions for these recommendations are found in the specific white papers. The recommendations provide useful information to both government funding agencies and industry for the purpose of defining individual and joint industry projects.

Materials

1. Corrosion resistant materials must be identified and tested for deep-water subsea equipment. A comprehensive materials database that classifies materials regarding deepwater corrosion mechanisms, material performance limitations, and galvanic interactions is needed. The data should include advanced materials.

2. A deepwater corrosion design philosophy must be established to reduce or eliminate locations of life limiting degradation on complicated systems. Special attention must be given to low cost components such as bolts, fasteners and electrical connectors.

3. In deep-water offshore structures, topside components have a high multiplier for weight reduction, thus a high potential for cost reduction. Examples of new applications in composite materials are in production; drilling risers, topsides flow lines, deck structures and process systems all have the potential for significant weight savings. Use of high strength light metals such as titanium alloys also applies.

4. The use of composite materials for ship structures should be expanded to achieve an optimal benefit. The corrosion behavior of these composites must be characterized and understood to allow for proper material selection.

5. The relationship between the ballast tank environment and the resulting corrosion damage demands study; corrosion protection systems and practices must be identified and evaluated. The seawater piping in the ballast tanks may be exposed to an environment more aggressive than anticipated at the design stage. Also, an awareness of microbiologically induced corrosion in water ballast tanks and in cargo tanks should be promoted.

6. Substandard weld quality of highly alloyed seawater piping on some floating production units gives rise to corrosion problems, and recommended welding practice needs to be established.

7. In the long term, the use of non-ferrous advanced materials as structural members may eliminate corrosion control cost. To take full advantage of currently available advanced materials, an extensive corrosion-testing program is required.

8. Improved technology transfer is needed in the manufacturing and use of duplex stainless steels and super-austenitic stainless steels.

9. Fiber reinforced polymers, known as FRP and GRP, require a more complete database on applications, models for predicting durability and QA/QC developments. Standardization for dimensions of FRP components is critical for industrial application.

10. Galvanic compatibility of stainless steel and carbon steel reinforcing bars in concrete used in harbor structures should be investigated.

11. The deWaard and Williams prediction methodology for CO_2 corrosion of steel is universally used. Additional work to further define its application limits will benefit the industry.

12. The nature of the sparking hazard risk associated with aluminum-bearing coatings needs investigation. The role of thermatic reactions and impact shock must be thoroughly understood. The sparking events should be quantified relative to the material combinations, impact energy and localized environment.

13. The susceptibility of TMCP steel to accelerated corrosion in tanker structures must be determined.

14. For the mooring systems, data on long-term behavior of different types of mooring lines are scarce, and work should be initiated to better document mooring lines performance. For chain links, several aspects require study. Studies should embrace possibilities for bacterially induced corrosion, and the possibility for corrosion fatigue of highly stressed systems. Also, the possibilities for long-term embrittlement effects on links, either when cathodically protected directly, or when draining current from the CP-system of the substructure, should be addressed. For steel wire ropes, the long-term reliability of the corrosion protection system should be documented, especially with respect to any sheathing that acts as a barrier against seawater ingress. The consequence of seawater ingress on hydrogen embrittlement effects should be investigated. For fiber rope systems, there is a general need to document the long-term behavior in seawater.

15. New materials and/or coatings for the splash zone area should be tested and evaluated. These data must be readily available to corrosion engineers.

16. There is a need to establish testing procedures which, in a reliable, reproducible and commonly accepted manner, document and qualify the corrosion behavior in seawater of different materials and components.

Design

1. A corrosion design philosophy for deep water subsea systems that addresses the following issues must be developed:

    1.1. Design should be made for much longer than field life. Over design to reduce risk of failure is desirable when economically feasible.

    1.2. Methods must be established to quantify cost versus risk in assessing system reliability. Risk-based material selection criteria can be developed.

    1.3. Project economic drivers should be established to balance initial versus lifetime cost.

    1.4. Hotspots on the complicated systems should be reduced or eliminated. Particular attention should be paid to low cost component details, such as bolts, fasteners, and electrical connectors.

    1.5. An integrated total system design needs to be provided and the system design should be simplified.

    1.6. Design guidelines for deepwater corrosion protection system selection are needed.

    1.7. Information on stray currents that may be control signals coming through the riser or intervention work-over lines can be captured, and this technology deserves further development.

2. Deepwater subsea equipment and facilities are complicated systems consisting of numerous materials operating under a wide range of conditions. The material compatibility of multi-phase systems is a design consideration, and design methodology to select materials for these deep-water applications needs to be established.

3. Coating and service inspection friendly designs for ship structures must be developed.

4. An optimal timing and design philosophy for retrofit of sacrificial anode systems should be developed.

5. The field of corrosion science should address the "people problem" in materials selection and corrosion control, as an important aspect of corrosion management.

6. Cathodic protection design guidelines for new deep-water pipelines should be developed.

7. Sufficient design information and test data should be more available to the engineers responsible for harbor structure. All requisite design equations must be provided.

8. There are many factors that determine the economic as well as the technical life of a marine structure. The additional first cost of measures to prolong the life has to be weighed against the present value of future repairs, and the costs of interruption of service during repairs. Recently, concerns over safety and protection have become of major importance. The net effect in most cases is the justification of more emphasis on durability, including quality control, and more emphasis on continuing maintenance during the service life. Investigation to develop a predictive model for cost of long term corrosion control for a structure, considering all the factors, is necessary.

9. The advanced method of corrosion control must be cost-effective. The owner/operator and the responsible engineer must both be convinced that the solution is cost-effective. In many cases, the facility must remain operational during the rehabilitation.

10. Pressure spectra of operating pipelines should be clarified.

11. In design/build contracts the corrosion engineer has even less input into the design. Technologies that have not been incorporated into industry or company standards are often ignored. An assessment of this barrier to advancement in corrosion engineering should be performed and recommendations must be identified which will quickly advance the corrosion protection of offshore structures, pipeline and ship structures.

12. The impetus to streamline the project development cycle reduces the opportunity to deploy and prove new technology, or even to properly apply old technology. The influence of this barrier on the long-term service life of the marine structures should be assessed.

Protection

1. Factors leading to microbiological induced corrosion (MIC) attack should be identified, investigated and developed to find an economical means to mitigate.

2. The expanded use of thermal spray coatings for commercial vessels should be explored and the suitability of thermal spray plastic coating for all vessels should be determined.

3. The ballast tank environment will be very aggressive to the corrosion protection system, and especially the coating. Temperature fluctuations and varying strain and movements of the steel substrate will require high flexibility and low tendency to embrittlement of the coating. These properties are presently not very well

documented for ballast tank coatings, and more data are needed to understand and document the aging properties of coating system candidates.

4. With respect to the external corrosion protection of the hull, the long-term aging and breakdown characteristics of the applied coating system, working in combination with an impressed current cathodic protection system, are not very well documented, and tests designed to provide such data seem to be of limited relevance. Methodologies to use cathodic protection with various combinations of coating materials and thicknesses should be developed.

5. The long-term operation of the CP-system within safe and predefined limits is a challenge with respect to an even current and potential distribution throughout the lifetime. This technology needs further investigation and development.

6. The arcing effects found on thruster systems due to stray currents must be examined and understood in order to specify preventive actions.

7. New technologies for cathodic protection should be tested and evaluated so that data is readily available to corrosion engineers for consideration.

8. Reliability of impressed current systems needs improved.

9. Automated collection of cathodic protection monitoring data from permanently installed sensors would allow more detailed troubleshooting of faulty systems, and might be accepted in lieu of drop cell surveys by regulating agencies. In service data acquisition systems need to be developed and used.

10. Development of models and data for projecting cathodic protection maintenance current density is needed.

11. The recently proposed slope parameter approach to cathodic protection design should be incorporated into recommended practices.

12. The optimal timing of, and design philosophy for, retrofit of sacrificial anode system needs development.

13. Factors that affect anode efficiency (e.g., temperature, resistivity, chemistry, etc.) require identification and characterization. Improved correlation for sacrificial anode efficiency as a function of composition, temperature, and anode current density and long-term exposure is desirable.

14. A more cost-effective means of retrofitting sacrificial anodes must be developed.

15. Improved prediction of coating breakdown with time is needed. Lower cost shop-applied coatings, and more reliable and effective field touch-up coatings need to be identified and evaluated.

16. Changes in offshore processing require a response in corrosion control. One example is the increased use of "inert gas" containing high oxygen contents generated on offshore facilities.

17. Cathodic protection design guidelines for new deep-water pipelines need investigation and development.

18. A state-of-the art review of pipeline coatings, including their characteristics and behavior in corrosive environments, should be prepared so that further advances are made with a benchmark.

19. Guidelines for the use of inhibitors and their selection with full consideration of flow regimes should be developed.

20. An investigation of coatings for internal corrosion control in flow times should be performed.

21. Anti-fouling materials, e.g. copper, and their possible corrosive effects on aluminum and steel, should be characterized.

22. The use of coatings on existing structures below the splash zone, has had limited success in the past; development of improved products and application techniques continues in this area. A standardized methodology to evaluate these coatings needs to be developed.

23. As cathodic protection of reinforced concrete port facilities becomes more common, installation issues such as "partial" reinforcement continuity, sprayed anode adhesion, and grouting materials for mesh and ribbon anodes should be investigated. Also, operational issues such as "effective" potential shift, current distribution, and the effects on high strength strand should be addressed.

24. Additives for corrosion control, the focus of earlier investigations, have recently received less attention in favor of reinforcement coatings and consideration of alternative materials for reinforcement. Although still used as "an extra measure of protection" their action is commonly misunderstood. Reputed corrosion "inhibition" or "passivation" in some instances is due primarily to simple inducement of accelerated curing, deterring ion migration in accelerated tests, rather than actual electrochemical process modification. Evaluations of the effects of admixtures used to alter workability, and the usefulness of inhibitors, sometimes accepted in lieu of strict quality control, need to be revisited.

25. Methods to protect dynamic deep-water risers should be established; suppression may lead to shielding of cathodic protection.

26. Corrosion control of thermally insulated pipelines for deep-water service requires study.

27. Data are required on cathodic protection interference/pipeline isolation at pipeline crossings.

Inspection

1. Corrosion monitoring systems, and sensors and devices for evaluation of protection systems during service need improvement.

2. Cost-effective methods for tank coating inspection, and for repair and maintenance for existing vessels should be developed.

3. Non-traditional pipeline design and construction should be evaluated to ensure that possible benefits are obtained.

4. State-of-the-art reviews are required on pigging and riser inspection (internal and external). A comparison of pegging and hydrotesting performance should be obtained and evaluated. An assessment of damage caused by hydrotesting needs to be addressed, and standards that set the minimum requirements of a pig should be established.

5. Standards for internal line pipe inspection are required.

6. Pipeline inspection should be identified as a critical issue.

7. A failure analysis database should be developed for the collaborative use of industrial and R&D organizations (universities, government laboratories).

Reliability

1. To justify deepwater subsea system reliability, a balance between system risk and system cost, should be established. The initial and lifetime costs of deepwater systems may define the feasibility of many subsea applications. Methods to quantify cost versus risk to assess system reliability must be established, and risk-based materials selection criteria must be developed.

2. The risks of corrosion damage should be quantitatively analyzed to reduce the conservatism of structural designs.

3. Internal pipeline corrosion modeling and prediction should be developed and used for risk analysis.

4. The effectiveness of cathodic protection on dynamic risers should be assessed.

5. Cathodic protection interference, using boundary element modeling and including effects of pipeline separation, should be assessed to show the effects of separation in comparison with the 12-inch separation required of on-land pipelines.

6. Application of formal fully integrated quality assurance programs and systems to control deficiencies in the corrosion control of pipelines should be investigated.

I. Corrosion Science

1. A fundamental understanding of the corrosion behavior in the deep water and subsea conditions must be developed if engineering based predictive models are to be established.

2. Mechanistic understanding of internal line pipe corrosion is needed to enhance the use of new corrosion protection approaches; i.e., inhibitors.

3. Cathodic protection, which has developed into a very effective corrosion protection practice, needs further understanding of its behavior relative to deep water and its use in conjunction with coatings.

4. Corrosion behavior of advanced materials (i.e., titanium, fiber-reinforced plastic, and high alloy materials) in seawater must be studied to achieve a fundamental understanding and to predict corrosion damage. Special attention should be given to the behavior of these materials in deep water applications.

Education and Training

1. The field of corrosion science should address the "people problem" in materials selection and corrosion control, as an important aspect of corrosion management.

Supporting Remarks

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SUPPORTING REMARKS FROM MINERALS MANAGEMENT SERVICE

~~MMS Supporting Remarks~~

~~By~~

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~~Galveston, Texas~~

~~February 9, 1999~~

Introduction and Welcome

On behalf of the U. S. Minerals Management Service (MMS), I would like to add my welcome to all of you here for this international workshop on corrosion control for marine structures and pipelines. I can see that by the number of participants as well as by the topics of the presentations on the agenda that this gathering will be a success.

I would also like to thank the organizers and the many co-sponsors of the workshop, especially Dr. David Olson and Dr. Stephen Liu, as well as other members of the staff from the Colorado School of Mines. A special word of thanks should also go to the other members of the steering committee for their time and efforts towards this event. The work of the individuals involved is easily measured by the successful manner in which the workshop commenced this morning.

Responsibilities of the MMS

Some of you may not be familiar with MMS. MMS responsibilities include leasing offshore lands for oil and gas exploration and development; collecting royalties for mineral activities on Federal lands; and promulgating and enforcing safety and pollution prevention regulations for offshore facilities. The Agency has a modest research budget but has been a significant player in some research areas to include as well control technologies, deepwater pipelines, abandonment of facilities, structures, oil spill response, and supporting facilities such as OHMSETT and the Offshore technology Research Center

Alan Abelson of Barrons, always a witty guy, commented on a former politician, saying "he had a lot of good ideas, but neglected to voice any of them." Well I can assure you that I have a lot of good ideas about corrosion but I'm just not going to voice any of them, other than to say that we're firmly against it.

Research Initiatives and Cooperation

We may not always get it, but we are smart enough to know that the strength of our research program is your ideas. That's why we organize workshops like these; and I think

they've been extremely successful. Thanks to Charles Smith, Research Program Manager for the MMS and other individuals such as Dr. Olson and Professor Bob Bea we seem to have had a number of excellent workshops addressing offshore technology issues. These workshops have been of great help in reviewing our regulatory programs and we seldom go against the guidance received (barring overriding political considerations).

First thing that comes to mind when I see the word corrosion is my '81 Toyota, which I purchased on Cape Cod when we had an office there. When I look back at '81, I'm startled at how the OCS program has contracted. At that time (plus or minus a few years) there were drilling operations in 3 regions of the Atlantic; in the Gulf of Mexico (GOM), Beaufort Sea, as well as a number of 9 rigs in the Santa Maria Basin offshore California.

OCS Oil and Gas Program

Despite the recent contraction of the program, the OCS is providing an increasing share of US oil and gas production. Presently, approximately 22% of the oil and 27% of the gas comes from the OCS and is the leading offshore gas producer in the world. Additional prospects for significant production increases elsewhere in the U.S. are slim. With oil and gas so cheap and plentiful, and not many people seem to upset by that, makes the stakes even higher from a safety/pollution prevention perspective. It's seems easier to some, not only to continue keeping future OCS areas off-limits, but to close the door further by limiting the opportunities for this industry to go about it job as it should. We can't afford safety disasters or pollution spectaculars that might threaten the GOM OCS program.

The industry just recently passed the 30th anniversary of the Santa Barbara blowout. Attention given to the blowout seldom centers on what has happened since it occurred, but more importantly, what has not happened since it occurred The attention given to the blowout is all about rallying the forces that are opposed to everything the offshore industry does, and those against offshore developments refuse to make the connection between their current lifestyle and the industry that helps supports it.

This industry has to rally too, not with rhetoric but by continuing to impress the world with the industry's technical achievements; achievements in the ocean that rival anything that has been done in space, and with a lot more near-term public benefits. In fact, the industry is getting favorable recognition about deepwater achievements, even in the Washington Post and Times.

You also need to impress the world with your safety and environmental record, with the way you manage your operations and your people - good times and bad - to achieve safety objectives. Your safety achievements may not impress the short-term traders on Wall Street, but if you're in this business for the long term, you know that safety management makes real good business sense as well as social sense. This industry, which

has suffered from public perceptions about safety and pollution prevention, must be at the vanguard in safety management, like it is in technology.

The thrust of our regulatory program has to focus on the fact that safety and pollution prevention issues are the operator's responsibility. The best we can hope to do as regulators are create a climate for industry achievements. We're gearing our regulatory program around your commitment. Our goal is not to have more regulations, more inspections, and more enforcement actions. Our goal is outstanding performance by the offshore industry. We want to give the top performers more latitude, and focus our inspection and enforcement resources on the problems.

We know that you operators and contractors have to be efficient, have to cut costs to survive in today's operating environment. But there can't be any letup on safety and protection of the environment. We want you to be efficient, to do things in the way that works best for your company. We are willing to work with companies on alternative compliance practices; but you have to be responsible, you have to be a top performer. Those that aren't will be seeing a lot of us and with a new rule we're about to publish could be disqualified from operating facilities.

The MMS is committed to doing what we can to minimize regulatory overlap. We are working closely with our counterparts within the Office of Pipeline Safety and the U.S. Coast Guard to see that regulations are not duplicated. We have recently signed mew MOU's with these agencies to outline the responsibilities that each will address to ensure that we do not have several agency requiring differing regulations.

Although there are divergent views on the best way to regulate (performance measures, safety cases, prescriptive rules, etc.), we try concentrate on two major issues. First we try to get out information on incidents for use by safety planners and secondly, we try to be a catalyst technology and operations achievement through workshops like this.

We don't focus on crises or perceived crises. There's no corrosion crisis, we have a number of concerns, but there's no crisis. However, corrosion is the leading cause of pipeline failures in the GOM. Most haven't caused safety incidents or major spills; nonetheless it can be a serious threat for future integrity issues. Anytime you have to repair a pipeline; there is a safety risk, not only that directly related to the repair itself. Look at what happened at platform SP 60 B in the GOM when a major explosion occurred while installing a pig trap for future inspections.

Conclusion

In closing, let me note that there are lots of outstanding companies and individuals in this industry. We want to learn from achievers that participate in workshops like these. We, as regulators, want to recognize those people and their organizations. Again, it has been a

pleasure to provide some opening remarks this morning. These are exciting times in the offshore industry and will require cooperation between all parties involved to maintain safety and protection of the environment. I can assure you that the MMS will work with you towards that goal. Thank you.

PETER Noble, Vice-President of Engineering

SUPPORTING REMARKS FROM A U.S. CERTIFICATION AGENCY

Phil ~~Mr~~ *B.* G. Rynn, *Manager of Ship Engineering*
American Bureau of Shipping

I would like to thank Dr. Olson and the Colorado School of Mines for inviting the American Bureau of Shipping to participate in this International Workshop on Corrosion Control for Marine Structures and Pipelines, and for inviting me to speak before this distinguished group. We look forward to the discussions and interchange of opinion over the next several days, and particularly to the conclusions and direction that the Workshop will provide in the area of corrosion protection of marine structures. These will undoubtedly be a great value to the marine industry and to other industries as well.

As you are probably aware, the American Bureau of Shipping is the primary American classification society and has as its mission promoting the security of life, and property at sea, and protection of the natural environment. ABS does this by setting standards for design, construction and operation, principally for surface vessels but for many other kinds of marine structures and systems as well. These standards also include survey of remaining material through in service measurement of thickness of marine structures, and so they have an impact on the topics under discussion at the Workshop.

Traditionally, sea-going steel vessels are surveyed periodically in port and where necessary in dry dock. Surveys are intended to ensure the vessel's condition is satisfactory for continued operation. Under certain circumstances steel must be renewed to return the vessel to a condition that is considered satisfactory for continued safe service. This approach has been fostered by the various public and private agencies entrusted with marine safety, such as the National and International Administrations, the Classification Societies, and the Underwriters.

The American Bureau of Shipping has a long history of interest in corrosion of ships and has over the years noted many attempts to minimize the affects of corrosion. Others have also had occasion to examine the effects of corrosion in the past. SNAME held a Corrosion Seminar in the early '50's to discuss the known effects of corrosion and methods to combat corrosion on tank ships. Their conclusion: " Corrosion control should be beneficial to the shipbuilding industry, as it will assist owners to establish available funds for new construction and replacement tonnage. All citizens and representatives of the industry have an economic interest in effective control, for the ravages of corrosion on military vessels are reflected in taxation, and on commercial vessels, their expense adds to the price of each gallon of petroleum product." At a subsequent SNAME annual meeting ABS presented a structural approach to tanker corrosion. The solution being a double hull design with limited structure in the cargo tank. I do not, however, have any evidence that this design had been built at that time.

ABS has been monitoring with corrosion for many years. In the '60's to encourage the use of protective coatings scantling reductions could be taken by the owner and ship builder. However, some vessels had coating breakdowns that resulted in excessive wastage of steel where extensive steel renewal had been required. The practice today is to have all ballast spaces coated. With the requirement to protect the marine environment tanker designs are double hull. In looking at the difference in both loading and stress patterns from single hulls structure, SafeHull is available to assess tankers today. The concern for corrosion prevalent in the marine industry is considered in this assessment by using the "net ship" concept which deducts a design corrosion margin from the as built structure to assess the stress for the vessel at a point in the future. Thus a ship design is examined at a point below the structural material used in construction.

A ship or other marine structure in service must be examined to determine that it has adequate material remaining to perform its function. This is done through cooperation of the owner and classification society by periodic surveys and measurement of the remaining material. Where material is found to be below acceptable levels steel renewal is necessary to return the vessel to a condition satisfactory for continued operation. Measurement of steel was originally done by gauging or drilling the steel to establish the thickness today the common practice is to use ultrasonic* measurement but there are many other methods currently being explored to establish the remaining thickness of the steel. Some of these may be deemed necessary to establish the suitability of many of the offshore structures being placed into service now and in the future.
A number of the structures designed for offshore operation will and are presenting some definite challenges for the operator and classification society. Some of the structures where new techniques or innovative application of present practice will be necessary are tension leg platforms, spar structures and deep draft caissons, and subsea installations.

Although the majority of ABS's business is concerned with classification of ships and offshore structures, the topics of corrosion with regard to inspection, monitoring, protection and risk are most important in ensuring the safety of the people, property and the environment. This is of course ABS' primary mission to the marine community and the public.

A review of the topics chosen for the workshop activity and the subjects for the theme papers shows that these Workshops will address the major challenges in corrosion mitigation, and also areas where successful results have been achieved that represent the state-of-the art and practice in corrosion control.

The American Bureau of Shipping fully supports the ongoing efforts in corrosion mitigation through design, maintenance and continued discussion of the topic. ABS encourages everyone here to actively participate, so that these Workshops will develop useful guidance for the direction of application, inspection and future

research. The commercial marine sector will benefit greatly with the advancement of and collation of corrosion control technology. It has been a pleasure to speak before you this morning to share our enthusiasm for this Workshop, and to briefly describe ABS's interest, experience and desired improvements in corrosion control of marine structures.

SUPPORTING REMARKS
"Corrosion Control for Marine Structures and Pipelines"

Robert W. Waldrup
Vice-President of Operations
Newfield Exploration

Today I am here representing the Offshore Operators Committee. This is a working group, which represents 77 general member oil and gas companies that conduct operations in the Gulf of Mexico. In addition our association membership includes 28 contractors and consultants with significant interests in the GOM. The group represents both large and small operators and is overseen by an Executive Committee which has representatives from the various operators and contractors. Our primary purpose is to work with the various governmental agencies to provide technical support and information on which they can base regulatory actions. We have technical subcommittees made up of anywhere from four to five people to larger subcommittees, which may include smaller subcommittees to tackle specific issues. Our constituency operates over 95% of the platforms in the Gulf of Mexico and drills over 95% of the wells. As operators and contractors in the Gulf of Mexico we are intimately familiar with corrosion.

Corrosion is something with which each operator lives with on a daily basis. It is something that can not be eliminated but it is something that can be controlled. The best time to control corrosion is up front in the design phase. It is provided for in the design of our platforms and drilling rigs. We install either sacrificial anodes or the use of impressed current systems to account for galvanic corrosion. Specialized paint systems are utilized. Special coatings are applied in splash zones to protect these areas. We add metal to certain areas to give added life. The design of our production equipment requires the use of anodes and treating chemicals to protect the equipment itself. Even the wells that we operate require that corrosion be addressed in their design. We use specialized tubulars such as 13 Chrome when we are faced with a carbon dioxide problem. In other instances companies have used downhole injection systems to provide a continuous treatment program. Finally, pipelines are designed to account for corrosion over their life through the use of coatings, wall thickness increases and sacrificial anodes. These are only a few of the ways that corrosion is addressed in the design phase of any project. In this conference, I am sure that you will discuss these and many more methods of designing for the control of corrosion. Design criteria for most of our equipment and wells is specified in the API Recommended Practices that are in wide use by the industry today.

Corrosion may be something with which we live on a daily basis but its biggest ally is time. Time allows the small incremental changes brought by corrosion in its various forms to build to larger and more serious effects. Therefore serious corrosion is the cumulative effect of much time and many small corrosive actions or reactions. One of the prime factors that must be developed in any design for corrosion is the life of the product. The expected life of the rig, platform or equipment is projected and then suitable methods of protection are applied to protect the equipment for its expected life. Most of the time the conditions are as predicted and the life is as predicted and the applied protection is sufficient. But sometimes conditions change. The life is greater than expected or the conditions are harsher than imagined. Then we must address the corrosion issue through secondary means. We might add sacrificial anodes, repaint certain areas to prevent loss of metal in critical beams, increase our chemical treatment program, or

apply an impressed current to replace the loss of sacrificial anodes. The monitoring of corrosion must be constant and pursued with diligence.

To date approximately 5500 platforms have been set in the GOM and 1600 or so have been removed. There are currently 3900 platforms left in place. Platforms have been installed on a regular basis for over 40 years. Some of the platforms have surpassed their original design life and are still in service. These platforms as a whole have stood the test of time. The design criteria which we used in the early days in the GOM was a long way from the current criteria but many of those platforms are still in good shape and are being used on a daily basis. This is because the industry made it our business to understand corrosion and build in safeguards or where necessary return to repair or retrofit the platforms and equipment. The platforms that are not in good shape must be identified and either retrofitted or removed.

One of the biggest issues facing the industry is to define what is good shape. Good shape to me does not mean that the platform needs to be in pristine condition or just like new. It does mean that the platform must be in a condition to provide protection to the people who work and live on the platform and for the wells and equipment located on the platform. Definition of what constitutes the protection needed will become one of the key issues in the future for GOM operators as our platforms and equipment continue to age. Hopefully, this conference will provide some insight into methods that might be used to determine the useful life left in our platforms and equipment and thus the industry will be able, on a quantitative basis, to determine the remaining life of any piece of equipment.

This week this conference will cover many of the aspects of corrosion control. This important subject is one of vital interest to the offshore oil and gas industry. I am sure that the dissemination of information to the participants will allow us to return to our respective organizations and do a much better job of planning for corrosion control in our business in the future.

Keynote Address from An International Offshore Industry-PEMEX experience on corrosion control for offshore facilities at the Bay of Campeche

Victor Valdes Rubio (M.Sc.), PEMEX Exploración y Producción, Gerente de la Unidad de Inspección, Mantenimiento y Logística, Región Marina Suroeste, Ciudad del Carmen, Campeche, Mexico.

Abstract

In 1978 as a result of extensive exploration work a huge reservoir was discovered, and named as Cantarell Field at the Bay of Campeche, this offshore area is located off the coast of Campeche and Tabasco states in the southeast of Mexico, and in those days its first drilled well was producing a record amount of 30,000 bpd. Nowadays, the total hydrocarbon production of the Bay of Campeche is 2 millions barrels of oil and 1.5 billion cubic feet of gas per day, this is 60% of the produced oil in Mexico. This production is handled by a pipeline network with an accumulated length of 2,500 km. with diameters that range from 8 up to 36 inches, and there are about 200 steel jacket platforms, 4 mooring buoys, and 1 Floating Storage Unit.

Sacrificial anodes are attached on steel jackets before those are installed in place as a corrosion control method for platforms, impressed current systems have not been used up to date for platforms neither pipelines. In the case of pipelines, the external corrosion control has been accomplished by employing sacrificial anodes in combination with a coating, and for the internal corrosion control some inhibitors have been injected in certain pipelines.

Pemex Exploration and Production carry out inspection programs on regular basis for platforms and pipelines to verify cathodic protection performance, and up to date corrosion control has been satisfactory, because no severe corrosion has been observed on Pemex facilities at the Bay of Campeche.

Introduction

In 1978 as a result of extensive exploration work a huge reservoir was discovered and named as Cantarell Field at the Bay of Campeche, this offshore area is located off the coast of Campeche and Tabasco states in southeast of Mexico. The drilling of its first well, and installation of Akal-C Drilling Platform, marked the initial point of the development of the Bay of Campeche, in those days that drilled well was producing a record amount of 30,000 bpd of oil. At the present time, the total hydrocarbon production of the Bay of Campeche is 2 millions barrels of oil and 1.5 billion cubic feet of gas per day, this is 60% of the produced oil in Mexico, and a large tax income for the Mexican government.

This production is transported by a pipeline network with an accumulated length of 2,500 km, and distributed as indicated in Figure 1.
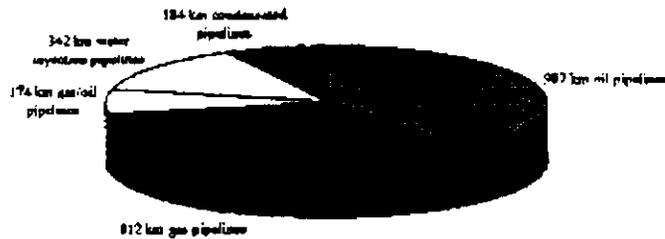

Figure 1, Accumulated length of pipelines

All the produced oil is transported to the shore by 3 pipelines of 36 inches diameter and 180 km length, and a fourth pipeline of 36 inches diameter and 82 km length, these pipelines arrive to Dos Bocas, Tabasco. Meanwhile, the produced gas is transported to the shore through 2 pipelines of 36 inches diameter and 82 km length to Atasta Compression Station, Campeche.

Additionally, there are 2 pipelines with 36 inches diameter, and 84 km length to transport oil to export sites located at the north of the Bay of Campeche, this site is called Cayo Arcas, in this place there are 2 mooring buoys. The operating temperature of most pipelines varies from 30 up 80 centigrade (there are few pipelines with an operating temperature of 100 centigrade), some of them transport sour fluids, and are buried with an average depth of 1 to 2 meters.

Pipelines are cathodically protected by sacrificial anodes which are supplemented with a pipeline coating such as; coal tar in the early days, and shrinkable tapes, and more recently Fusion Bonded Epoxy, over the pipeline coating a concrete coating is applied on fabrication yard to make stable the pipe under hydrodynamic loads due to waves and currents.

For submarine pipelines the most common anode that has been used are aluminum anodes (Galvalum-III type) with a chemical composition of aluminum-zinc-indium, and the typical anode separation for a 20 inches pipeline is every 84 meters (7 joints), this separation depends on selected anodes weight.

All the platforms installed in the Bay of Campeche are steel jacket type (in the Figure 2, it is shown a distribution of existing platforms), and are located in water depths from 20 up to 80 meters. The platforms are dedicated mainly for drilling wells, accommodating process and pumping equipment, and quarters for over 127 men. The platforms are categorized as follows:

- Drilling
- Compression
- Production
- Gathering
- Quarters
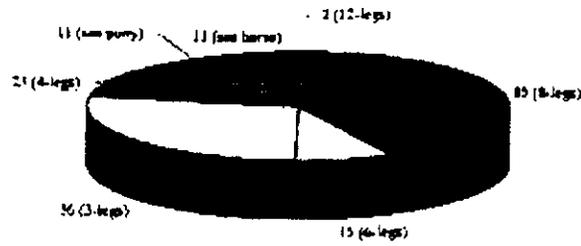
Figure 2, Number of installed platforms classified by number of legs

In Figure 3, it is shown a typical platform arrangement at one of the several platform complexes.

Figure 3, Typical platform complex

Corrosion control in the splash zone of platforms and pipelines

The splash zone is the most critical area of protection due to alternate wet and dry condition. In this splash zone a coating called RE-32 (epoxy 100% solids) has been applied by Pemex Exploration and Production with satisfactory results, so far no severe or localized corrosion has been detected during regular inspections of platforms.

In the splash zone of risers the external corrosion has been detected in previous inspections having a high rate due to mainly elevated operating temperature (most commonly from 50 up to 80 centigrade). In spite of this Pemex Exploration and Production has implemented a casing designed specially for this splash zone, which reduces the corrosion rate at a minimum value. The casing is made up of carbon steel, with a special resin that fills up the annular space between the riser and casing, allowing with this diminishing the elevated temperature on the casing, therefore the coating performance on the casing is not affected by temperature.

Corrosion control in the submerged zone of platforms

The submerged zone of all platforms are cathodically protected by aluminum anodes, these are cast on a typical 2 inches pipe core, which are welded to the template section during construction at the fabrication yard. The aluminum anodes that were used in the early days had a composition of aluminum-zinc-mercury, and in recent years aluminum-zinc-indium has also been utilized for having more capacity to drain current.

Pemex Exploration and Production has been conducting an annual inspection program for each platform, for detecting some structural damages. Divers carry out measurements of the potential difference between the platform with a portable electrode (silver-silver chloride reference electrode), as part of structural platform inspection. These readings are measured at previously selected points; usually at nodes with high level stresses, shielded areas, conductor guides, and at anodes, in order to inspect the 20 percent of platform nodes every year, covering the whole platform until the fifth year inspection.

Also, a visual inspection of anodes is carried out by divers, including removing fouling and corrosion products prior to potential measurement at anodes, typical measurements of anodes consumption have been found to be 5% of their original volume. Unfortunately some of these anodes may become passivated after several years or deliver considerably less current than nominal, but this has occurred rarely.

The following conditions would normally indicate more frequent measurements, during the inspection task:

- Marginal protection observed at certain areas
- Modifications made to the cathodic protection system or steel structure

The following conditions may indicate less frequent measurements:

- Satisfactory protection of steel (more negative than -850 mV versus Ag/AgCl)
- Steady consumption rate of anodes

A large amount of potentials has been collected for each platform along these 20 years, and by statistical analysis it could be possible to optimize the frequency of inspection of the cathodic protection systems by Pemex Exploration and Production in the near future.

A potential survey is one of the most valuable methods to inspect the corrosion condition of steel structures. This method is relatively simple and its main advantage is that it is easily applied to cover large parts of platforms, another advantage is that the acceptance criteria has already been well established. If the measured potential is within the protective range it is quite sure that no extensive corrosion will take place, on the other hand if the measured potential is outside this range serious damage is bound to occur unless corrective actions are taken.

Pemex Exploration and Production follows the most widely accepted criteria for cathodic protection as established in NACE Standard RP 0176 "Corrosion Control of Steel, Fixed Offshore Platforms Associated with Petroleum Production", is a structure potential more negative than -850 mV versus Ag/AgCl electrode.

As most of the platforms are located in shallow waters, Pemex Exploration and Production did not have the necessity of contracting an ROV for potential measurements on platforms.

External corrosion control for submarine pipelines

In the early days Pemex Exploration and Production performed the cathodic protection inspection of pipelines by using the towed fish/trailing wire method. In this method a test connection to pipelines had to be done, usually at an accessible location such as at a riser, a reference electrode (Ag/AgCl) is towed above the pipeline from a vessel while maintaining the test connection. The pipe to electrolyte potential was measured and recorded on board with a computerized data acquisition system, the position of the reference electrode "fish" relative to the as built coordinates of the pipeline was achieved by using the vessel sonar system, which also was equipped with a position system.

The objective of this type of inspection was to determine the general level of cathodic protection relative to NACE criterion of -850 mV versus Ag/AgCl. Potential profiles recorded using the towed fish/trailing wire method typically had a smooth shape; this is due to low resistivity of the sea water and averaging effect caused by the semi remote nature of towed fish. This survey provides general information to determine magnitude and direction of long lines currents, electrical interference, and current requirements. This inspection method has been abandoned, and now ROV assisted remote electrode are carried out to cathodic protection inspection.

Comparison of data collected using the towed fish/trailing wire method with data recorded using an ROV on the same pipelines has shown that the overall measured potential level were in general terms with roughly the same value. However, the primary difference is that with the towed fish/trailing wire method was not possible to detect anomalies such as coating holidays, low potential, missed and passivated anodes.

ROV assisted remote electrode inspection

By employing this method the potential between an Ag/AgCl electrode, and a pipeline is continuously measured by the difference between an electrode positioned just above the pipeline(held by the ROV arm), and a remote electrode located near the water surface. These measurements are used in conjunction with direct contact potential measurements at anodes or at any accessible locations along pipelines.

At the starting point of a remote electrode survey, a direct contact potential is measured at an accessible location such as a bracelet anode. Simultaneously, the potential between the electrode close to the pipe and remote electrode mounted on the submersible umbilical is recorded. This establishes the fixed voltage offset between the pipe potential and remote earth.

Recently, Pemex Exploration and Production has done a great effort in inspecting 45 pipelines by using ROV assisted remote electrode inspection. The inspection of the cathodic protection systems reveals that most of the pipelines have a pipe to electrolyte potential more electronegative than the permissible indicated by NACE. However, as a conclusion of this inspection program, a few of these pipelines show some coating holidays, and low pipe to electrolyte potentials, also in areas with good visibility some anodes were detected with a consumption greater than average.

At the same time it was implemented a program to inspect by smart pigs those pipelines which are considered as strategic. Strategic pipelines are those which are essential to transport the gas or oil to export sites or processing plants at land.

The approximate accumulated length of inspected pipelines by smart pigs from 1991 up to date is approximately 400 km, and all of them have been gas pipelines.

The reason for not inspecting additional pipelines is the limitation on capability of smart pigs on being used on oil-gas pipelines operating at elevated temperature (almost 80 centigrade), and because there are some pipelines in which some work has to be done to modify their pig traps to accommodate last generation smart pigs, another reason is because some pipelines have lateral tie-ins, in which is not possible to run a pig.

As an example, it is presented the correlation between the external corrosion detected by a last generation smart pig (flux leakage technique), and the pipe to electrolyte potential measured by ROV assisted remote electrode inspection.

The smart pig reports 317 anomalies, with a maximum metal loss of 31% of nominal thickness for the whole length (20 km), within this total are included anomalies classified as metal loss due to internal and external corrosion, and those attributed during pipe fabrication.

In figure 4, it is shown all the reported external corrosion; along the horizontal axis it is shown the pipeline length (only 4 km) , and in the vertical axis the external corrosion, which is represented with small rectangles, as a percentage of the nominal thickness. It should be noticed that only external corrosion was included, and metal loss due to internal corrosion and fabrication faults were discriminated.

In figure 4, it can be observed that the external corrosion is concentrated at certain points along the segment of 4 km, and that the maximum value is about 18%.

With the idea of correlating the external corrosion versus the potential profile, both graphs were overlapped, and by means of this it could be corroborated that external corrosion was taking place at areas where the ROV assisted remote electrode inspection indicated less electro-negative potentials.
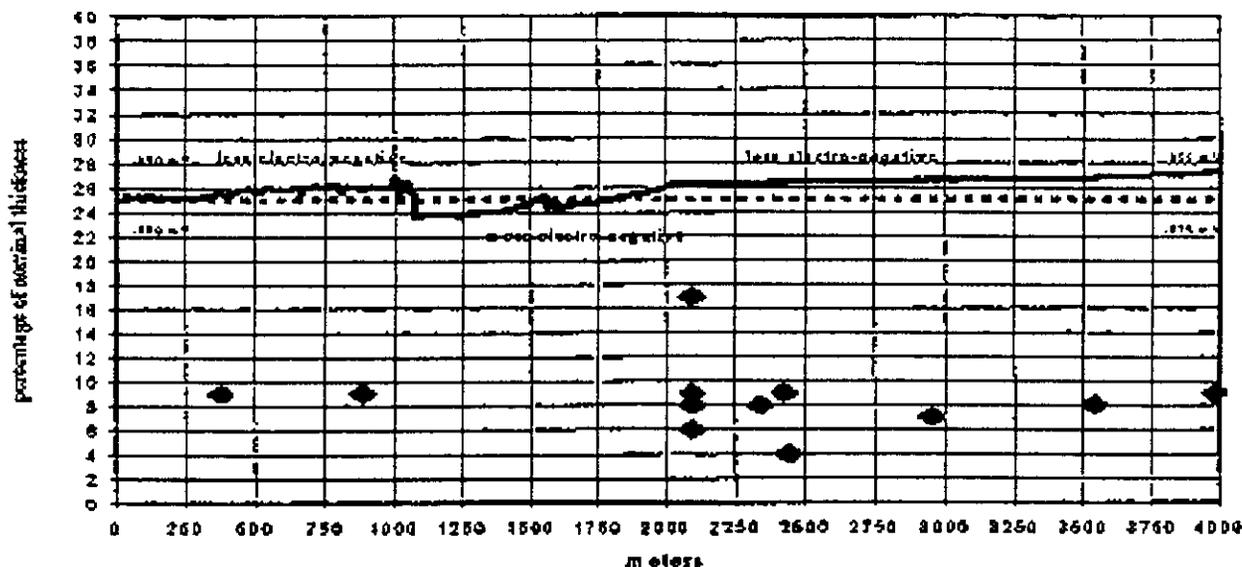

Figure 4, Correlation between external corrosion and pipe to electrolyte potential profile

Internal corrosion control for submarine pipelines

Nowadays, the corrosion inhibitor that are been used in the pipelines at the Bay of Campeche, are water-based, dispersible in hydrocarbons, and generally amide type inhibitor, since after laboratory and field tests these inhibitors have proved to provide satisfactory internal protection.

The parameter that Pemex Exploration and Production uses to determine if a inhibitor has to be injected in a pipeline is the pipeline corrosion rate, if the measured corrosion rate is higher than the permissible (3 mpy), then a inhibitor has to be injected. In the Figure 5 it is shown a typical record of the internal corrosion rate of a gas pipelines.
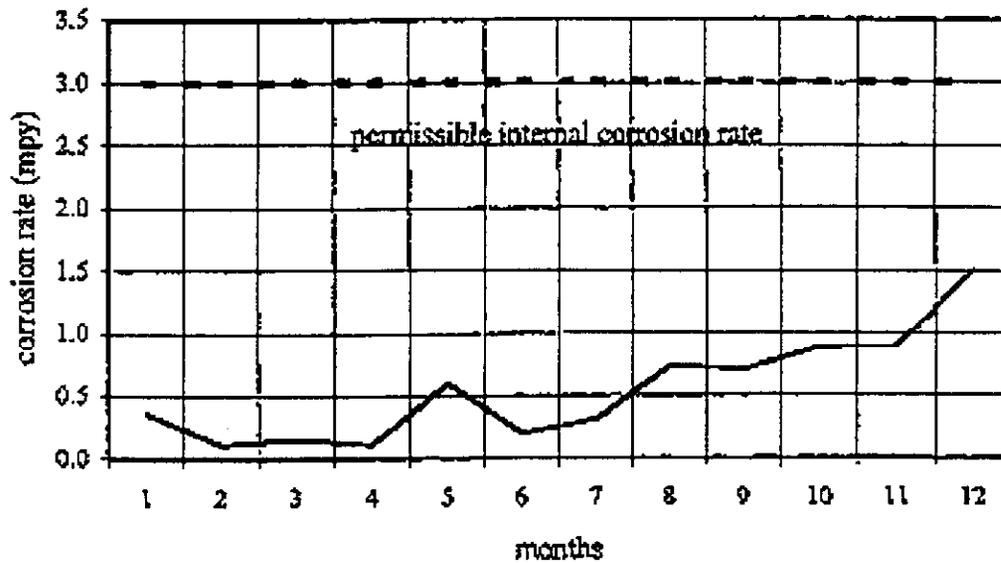
Figure 5, Typical internal corrosion rate of pipelines

The technique of weight loss during 30 days has been carrying out by Pemex Exploration and Production for internal corrosion inspection of pipelines. Since 1996 Pemex Exploration and Production has implemented a program for continuously monitoring the corrosion rate of pipelines by using a data acquisition system on board at the platform.

Conclusions

So far the corrosion control methods that have been employed in protecting the offshore facilities have been adequately taken, because severe corrosion has not been found in the offshore facilities at the Bay of Campeche.

However, inspection by smart pigs has to be carried out in those pipelines that transport crude oil, and mixtures of gas-oil, and which are operating at elevated temperature, as smart pigs have been used only on gas pipelines.

As the pipelines are aging the coating is having more holidays, and the probability of corrosion is increased if the cathodic protection performance is not satisfactory, therefore new procedures for designing of retrofitting systems are needed specially for pipelines operating at elevated temperature.

The remaining life of sacrificial anodes of pipelines operating at elevated temperature has to be estimated, based on laboratory and field inspections.

New technologies have to be implemented in the internal corrosion control by injecting inhibitors, which are environmental friendly.

Keynote Addresses

Deep Water Corrosion Fundamentals
J.F. Jenkins, Nickel Development Institute
B. Mishra, Colorado School of Mines

Risk and Reliability Analysis of Corrosion of Marine Pipelines
R. Bea, University of California, Berkeley

Inspection of Pipelines Based on Reliability
J. Matias Acevedo, Instituto Mexicano del Petroleo

DEEP WATER CORROSION FUNDAMENTALS

James F. Jenkins, and Brajendra Mishra
Nickel Development Institute
Toronto, Ontario, Canada
Colorado School of Mines
Golden, Colorado, USA

Abstract

Mankind has been interested in the deep-sea environment primarily for two reasons, (i) to resolve the mysteries of life in deep water and (ii) to explore the sea bed for resource recovery, such as natural gas and oil. Both these ventures have required the development and use of special materials that can withstand the complex deep water environment. This paper attempts to describe the salient differences between the deep water and sea-level environments and the influence of these differences on the behavior of materials. Fundamentals of the corrosion science in deep water have been discussed and the demands placed on the engineering of materials have been explained. Besides the appropriate selection of materials, other means of corrosion protection in the deep ocean environment have also been highlighted.

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are in the
"original"
package.

Introduction

The ocean is an extremely aggressive environment. Through combined action of chemical, biological and physical action, it places structures and equipment exposed to the marine environment at serious risk. Man has learned to design and build structures that survive in the marine environment through many years of experience, both good and bad. However, human experience has been primarily limited to the near-surface marine environment.

Man's exploration and exploitation of the deep ocean has been a very recent and limited adventure. Man first began to explore the deep ocean in 1934 when William Beebe and Otis Barton used a tethered bathysphere to reach a depth of 923 M (3028 ft.). In 1960, the bathyscape Trieste, manned by Dr. Jacques Piccard and Lt. Don Walsh, reached the deepest ocean depths with a dive to 10,912 M (35,800) feet in the Marianas Trench [1]. This depth has not been reached since. There are currently no manned submersibles capable of reaching these depths. Much of the manned presence in the deep ocean has been supplanted by the use of unmanned vehicles. The early impetus for exploration of the deep ocean was defense interests, but today it is also driven by human exploitation of the mineral resources in the deep sea.

Corrosivity of the Marine Environment

The marine environment damages many materials through chemical and physical interactions with the environment. This damage may be caused by chemical interaction, commonly called corrosion, by physical damage or through attack by biological organisms, or a combination of these interactions. The characteristics of the marine environment that govern these interactions can be grouped into three broad categories, physical, chemical, and biological.

Important physical characteristics of the marine environment that cause the deterioration of materials, include factors such as electrical conductivity, temperature, ocean currents, waves and tides, and physical characteristics of the seafloor.

The high electrical conductivity of seawater promotes the electrochemical reactions that are responsible for the corrosion of many metals. The specific conductance of seawater varies somewhat with location, but is generally in the range of 0.03 $\Omega^{-1} \cdot cm^{-1}$ [2]. This high conductivity promotes all types of corrosion activity including general corrosion, galvanic corrosion and pitting.

The temperature of the environment has several effects on corrosion. Increased temperatures increase the conductivity of seawater. Many corrosion reactions are limited by diffusion. Increased temperature increases diffusion. A temperature increase of 10 ^0C (18 ^0F) commonly doubles the rate of diffusion [3]. However, temperature also affects other important parameters such as dissolved oxygen content. The dissolved oxygen content of seawater in equilibrium with the atmosphere is lowered by an increase in temperature. Dissolved oxygen levels have a complex effect on the corrosion of metals. When the rate of corrosion is controlled by the rate of oxygen reduction at the cathode, such as is common for corrosion of steel in neutral or alkaline solutions, increased oxygen availability will increase the rate of corrosion. On

the other hand, materials such as stainless steels that rely on an oxide film for their corrosion resistance may be adversely affected by limited oxygen availability.

Ocean currents can affect the corrosion of metals directly through velocity effects and indirectly through the effect of the currents in bringing ocean masses with varying chemical characteristics to the exposure site. An extreme example of the effect of ocean currents on corrosion is in the Cook Inlet in Alaska. High tidal currents in the inlet increase the current demand for cathodic protection of steel from a typical value of 100 mA/M^2 (9 mA/Ft.^{2}) for a structure not exposed to high tidal currents to over 400 mA/M^2 (37 mA/Ft.^{2}) [4]. Ocean currents also affect other characteristics of the seawater at a specific site by bringing waters with different characteristics such as temperature and salinity to the site. These currents can vary seasonally or, like the El Niño currents, may occur sporadically.

Waves and tides produce direct velocity effects similar to those noted above for ocean currents. Wave loading on structures can by very destructive, particularly during storms, which combine loading from extreme wave action and high winds. The distribution of corrosion on steel structures extending through the tidal zone illustrates the effect of the environment on corrosion and the interaction between steel exposed to different environments. Figure 1 shows a typical profile of corrosion rate versus height for a structure exposed from the mud line to full atmospheric exposure [5]. In the atmospheric and splash and spray zones, the distribution of sea salt and the high availability of oxygen cause high corrosion rates. In the intertidal zone, corrosion rates are low due to the oxygen concentration cell between the intertidal zone and the fully immersed zone directly below. The high oxygen levels in the intertidal zone cause the steel in this area to be cathodic to the steel in the fully submerged zone. This has the effect of reducing corrosion in the intertidal zone and increasing corrosion in the upper part of the fully immersed zone.
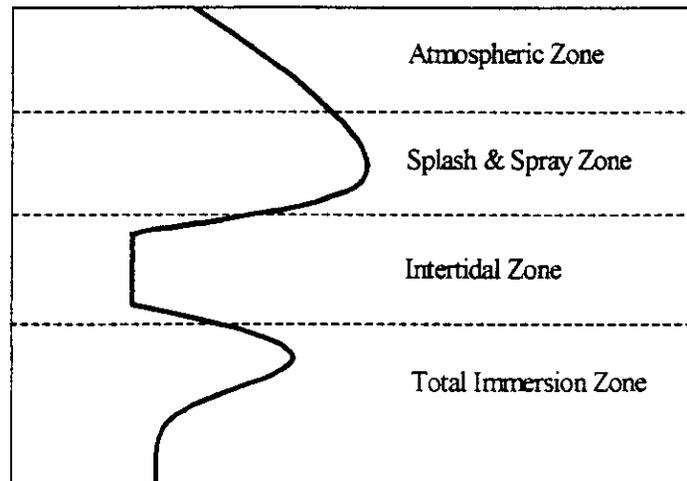

Figure 1. Corrosion profile of steel in tidal exposure.

Biological organisms can also affect materials physically. The film of organisms that attaches to surfaces in marine environments inhibits diffusion [6]. Organisms can also damage protective coatings and hard-shelled organisms such as barnacles can create differential

environment cells resulting in crevice corrosion [7]. Wood or other organic materials can be attacked by organisms such as limnoria that directly metabolize the materials or organisms such as teredo that bore into the materials primarily for protection. Even concrete can be attacked by organisms such as pholads that naturally bore into rock for physical protection and have little preference for rock over concrete. Other organisms, such as sea urchins, "graze" metal surfaces keeping them free from corrosion products that would otherwise inhibit corrosion [8].

The physical characteristics of the seafloor sediments can also affect the deterioration of materials. Much like the situation on land, the grain size and packing factors of the sediments affect diffusion through the sediments and this affects the availability of oxygen and other corrodents. The physical characteristics of the sediments also affect their electrical conductivity. In some cases, diffusion is so limited that anaerobic conditions are achieved and obligate anaerobes such as sporovibvrio desulfuricans can become active. These organisms produce sulfides that can have a dramatic chemical effect on materials as described below.

Chemical characteristics of seawater also have significant effects on the deterioration of materials. These characteristics include dissolved inorganic and organic matter as well as dissolved gases, pH and alkalinity. Biological organisms and the physical characteristics of the seafloor also affect the chemical makeup of the environment.

Seawater contains a wide variety of dissolved inorganic mater. Of this, the chloride ion is perhaps the most important with regard to the corrosion of metals. While metal oxides have only limited solubility in water, metal chlorides are generally much more soluble. While insoluble oxides can form films that are either extremely protective such as the passive films formed on stainless steels or partially protective such as the rusts formed on steel, soluble chlorides cannot form effective protective films [9]. Chlorides are also primarily responsible for the high electrical conductivity of seawater described above. Other ions in seawater such as sulfate and nitrate can affect corrosion reactions, particularly the formation of protective films.

Dissolved oxygen is a very important factor in the corrosion of metals in seawater. Oxygen plays a primary role in promoting the cathodic oxygen reduction reaction that predominates in neutral and alkaline solutions. Oxygen is also an important factor in the stability of passive oxide films that are important in the performance of materials such as stainless steels and aluminum alloys. As described above, the solubility of oxygen varies inversely with temperature. Carbon dioxide is also present in seawater and affects the pH and alkalinity of the seawater. pH can have direct chemical effects, particularly on metals such as aluminum [10] and can also affect the deposition of carbonate films that significantly reduce corrosion and cathodic protection current demand [11]. pH of surface waters generally falls within the range of 7.5 to 8.3 in unpolluted open ocean waters [12]. Seawater is well-buffered [13], and has an alkalinity in the range of 22 mg-atoms/L [14].

Non-living organic matter in seawater is strongly adsorbed on surfaces and has a significant effect on corrosion [15]. This material forms a continuous film that can inhibit diffusion and also serves as a substrate for the attachment and growth of both microscopic and macroscopic marine organisms. These living organisms affect corrosion can affect the deterioration in many ways, both physical as noted above, and chemical. Chemical affects

include the excretion of organic acids that can accelerate corrosion [16] and, under anaerobic conditions, the production of sulfides that form non-protective films.

Seafloor sediments can be anaerobic and growth of obligate anaerobes can produce sulfides and other species that interfere with passive film stability. The chemical and physical characteristics of marine sediments are highly local. Many sediments, particularly those in tropical locations, are alkaline. Oxygen contents in the sediments are lower than in the seawater above. The local difference in oxygen content can drive oxygen concentration cells similar to those experienced in tidal corrosion with the corrosion rate just below the sediment/water interface experiencing increased corrosion. This effect has, however not been found to be predominant and corrosion of steel in the bottom sediments is usually lower than in the seawater above [17]. The opposite effect is noted for aluminum alloys [18] and stainless steels [19] where the effects of reduced oxygen in the sediments are detrimental.

The Deep Ocean Environment

The word "deep" is subjective when applied to the ocean. There is no set delineation between deep and shallow ocean environments. There are, however, several environmental factors that commonly vary with depth. Among these are the penetration of sunlight, dissolved oxygen content, pH, temperature, the number and type of biological organisms and hydrostatic pressure.

Sunlight penetration affects the deterioration of materials primarily by affecting the type and distribution of organisms. In the euphotic zone, typically from the surface to a depth of 80 M (260 ft.) sunlight penetrates readily, but its intensity decreases with depth and the penetration of red light is more attenuated than that of blue, green or yellow light. Both plants and animals thrive in the euphotic zone [20]. In the disphotic zone, between 80 to 200m M (260 – 650 ft.) little light of any wavelength penetrates and plant life cannot actively photosynthesize [21]. The aphotic zone lies below the disphotic zone. It is populated only by carnivores and scavengers [22]. The depths of these zones are variable with location and time. The values given are for clean open-ocean waters. On of the authors (Jenkins) suggests that, due to the dramatic changes in the accumulation of fouling organisms in the disphotic zone, the deep ocean begins here.

Oxygen content varies with depth in most ocean locations. In Figure 2, the profile of oxygen content with depth, at a site in the Pacific Ocean off the coast of Southern California is shown. At this site, the oxygen content falls with depth to a minimum at about 700 M (2300 ft.) and then increases with further increase in depth. This is typical of many sites in the Pacific Ocean [23]. At other sites, particularly in the Atlantic Ocean and Gulf of Mexico, the profile is similar. However, at warm water sites, the surface oxygen is lower and below the oxygen minimum zone can actually increase above the levels at the surface as shown in Figure 3. [24]

It should be noted that the variation of pH with depth follows closely that of oxygen content. In fact, the two are related by the combined effects of photosynthesis and other biological activity [26]. This provides a problem for the separation of the effects of oxygen content and pH on the corrosion behavior of metals in deep ocean environments. Are differences in corrosion behavior primarily due to differences in oxygen content or pH ?

Oxygen Content (mL/L)
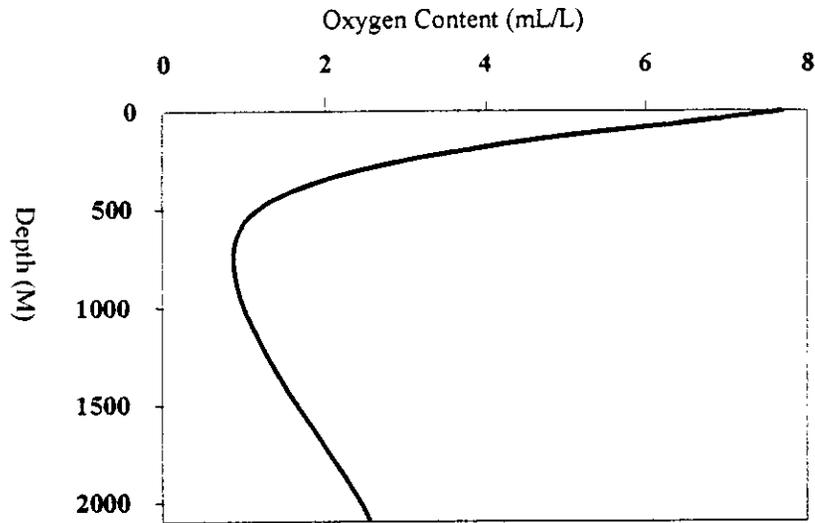
Figure 2. Oxygen profile with depth – Pacific Ocean site.

Oxygen Content (mL/L)
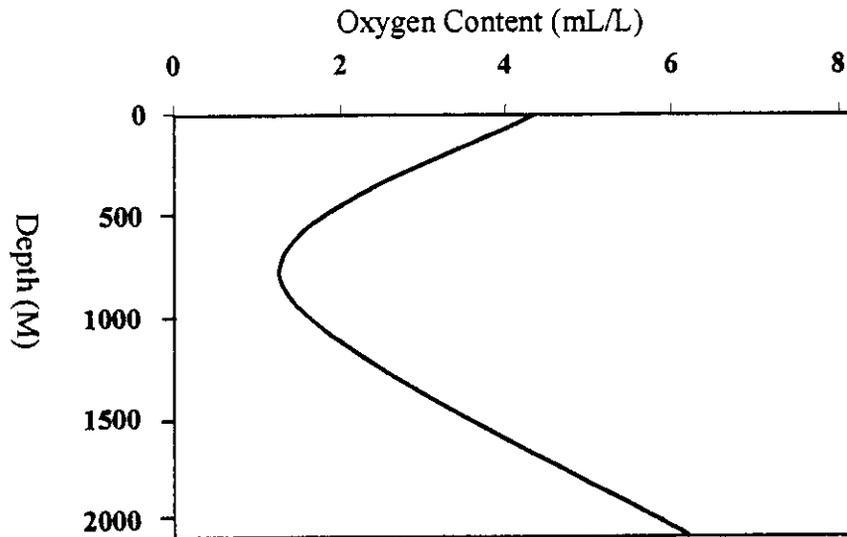
Figure 3. Oxygen profile with depth, Atlantic Ocean site.
pH follows a similar profile with depth as shown in Figure 4.

The answer to this question cannot be resolved by in-situ corrosion testing. However, from an engineering standpoint, if the oxygen content is known, the corrosion behavior can be predicted, even without a thorough understanding of the processes involved. Th pH of the seawater above alkaline bottom sediments can be anomalously high for some distance above the sediments depending of ocean currents.

Temperature of the ocean also varies with location and depth. Although there is a considerable seasonal variation of temperature near the surface, these differences decrease with

depth where the water is constantly cold and in the range of 1–4°C (34–40 F) [26]. A typical profile of temperature versus depth is given in Figure 5. [27].
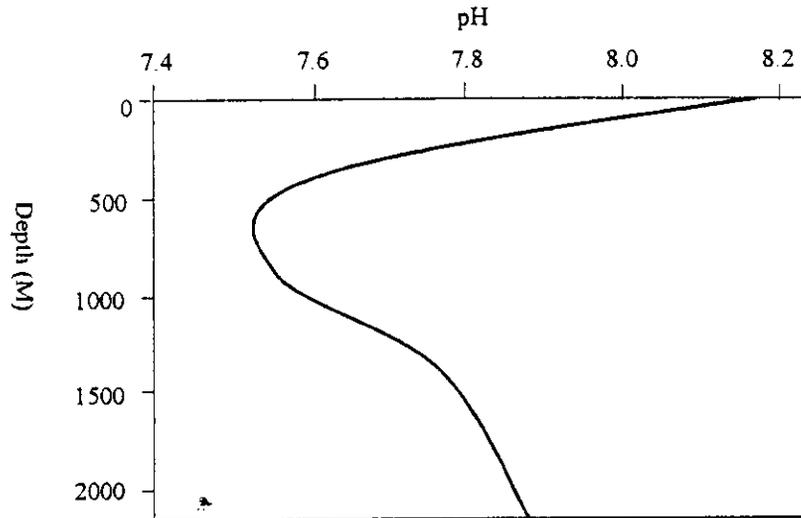

Figure 4. Profile of pH with depth – Pacific Ocean site.

As mentioned above, the number and types of organisms found in the deep ocean are very different from those found in near-surface waters [28]. While there are bacteriological slimes in deep ocean waters, the number of macro-organisms is significantly less in deep water. It is surmised that many of the species common to shallow water that are found at depth on manmade structures attached to the structure while the structure was near the surface and have managed to survive at depth. Many deep ocean animals live in or near the bottom sediments where detritus from above accumulates and is used as food [29].
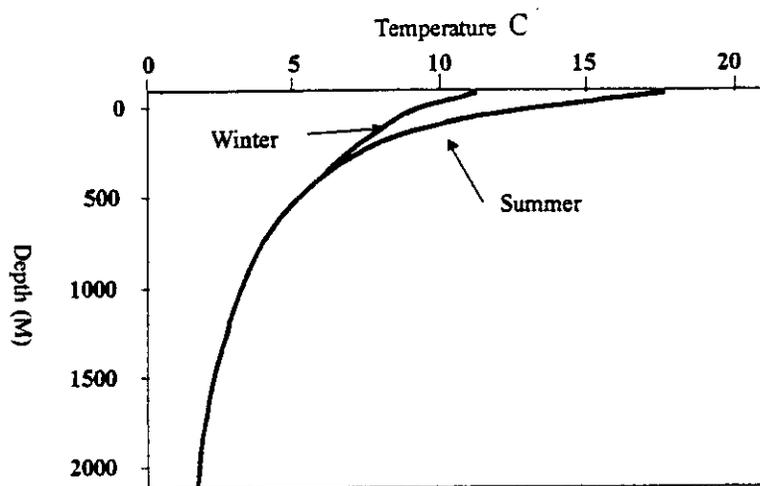

Figure 5. Profile of temperature with depth – typical temperate site.

Hydrostatic pressure is a major barrier to man's presence in the deep ocean. Pressure increases almost linearly with increasing depth. At the most extreme depths, pressures can

exceed 11 MPa (16,000 psi). [30]. At shallower depths, man can withstand the external pressure if specialized breathing gases are used and long decompression times can be accommodated. For depths in excess of a few hundred meters, man must either provide a pressure barrier between himself and the ocean, or rely on remote presence through robotic craft.

Electrochemistry under deep-water conditions

The possibility of corrosion is determined by the thermodynamics where as the rate of corrosion is controlled by the kinetics. The thermodynamics of corrosion is dictated by the Nernst Equation where the expression for any half-cell reaction may be shown as:

$$e = e^{o} - (RT/nF) \ln K \qquad (1)$$

where the half-cell potential, e, is dependent on the standard half-cell potential, e^{o}, the temperature, T, and the activities of the reacting species and corrosion products that determine the rate constant, K. R and F are the universal gas constant and Faraday's constant, respectively. For any given half-cell reaction, the number of electrons involved, n, also does not change. The standard half-cell potential is a constant for an electrochemical reaction at a given temperature.

Figure 6: Galvanic Series for metals and alloys in sea-water.

The basic principle for the establishment of galvanic cells, which is dependent on the presence of dissimilar metals and alloys (different e^o values) in a corrosive environment, is not influenced by the different deep-water conditions of temperature, pressure and ionic activities. Thus, the phenomenon of bi-metallic corrosion will not be any different in deep sea from other atmospheres. Figure 6 shows the galvanic series for common metals and alloys in sea-water. As a thumb-rule, combinations or galvanic couples of metals and alloys, placed widely apart on this chart, ought to be avoided, if possible. The greater the difference in the nobility of the alloys, larger is the driving force for galvanic corrosion.

A close examination of Equation (1) reveals that the half-cell potentials can be altered, i.e. possibility of corrosion can change, if the temperature or the activities of species should change. These factors do change under deep-water conditions. A pressure change influences the activity of gaseous species, such as oxygen and hydrogen, and the enormous volume of solvent affects the ionic concentrations. Every thirty-four feet of water causes the pressure to increase by one atmosphere.

The equilibrium predominance area diagram, known as the Pourbaix's Diagram, determines the potential as a function of solution pH. Regions of immunity, corrosion and passivity can be identified on this diagram. Figure 7 [31] shows the Pourbaix's diagram for iron in water at room temperature of 25°C and various ionic activities of iron, a_{Fe2+}. The concentration of other ions involved in the corrosion reaction will also cause the lines on this diagram to shift.

Figure 7: E vs pH (Pourbaix Diagram) plot for iron in water

Figure 8: Effect of temperature on Pourbaix's Diagram for $Fe-H_2O-CO_2$ system

It is evident that an increase in the ionic concentration enlarges the zone of passivity. It may be realized that under deep-water conditions, ionic concentrations are expected to be very low due to the enormous solvent volume. Such a decrease in ionic concentration will cause the region of passivity to shrink, or in other words, the regions of corrosion to expand. This aspect may be visualized in another way. High ionic concentration will cause the solubility limit of the solute ions to be reached faster. Thus, further generation of metal ions can be impeded causing an enlarged passivity region.

The role of temperature is evident in Figure 8 [32], which shows the Pourbaix's diagram for the $Fe-H_2O-CO_2$ system. An increase in temperature of 25° shows the partial collapse of the passive region. By the same token, a decrease in temperature in deep-water should expand the region of passivity or decrease the areas where corrosion is supported. It is cautioned that these diagrams are equilibrium diagrams, and as such, assumes the achievement of equilibrium.

The effect of gas pressure influences the possible cathodic reactions in deep-water. Figure 9 shows the stability of water as a function of pH. At active potentials water is dissociated into hydrogen gas where as, oxygen is generated at relatively noble potentials at any given pH value.

The influence of hydrostatic pressure can be examined for the reactions where hydrogen or oxygen is involved by the following cathodic reactions:

$$2H^+ + 2\,e^- \rightarrow H_2 \qquad\qquad (2)$$
$$2H_2O + O_2 + 4\,e^- \rightarrow 4OH^- \qquad\qquad (3)$$
$$2H_2O + 2\,e^- \rightarrow 2OH^- + H_2 \qquad\qquad (4)$$

Figure 9: Effect of pressure on the stability of water shown on E vs pH plot

Considering the generalized half-cell electrochemical reaction in the form:

$$aA + mH^+ + ne^- = bB + d\ H_2O \qquad (5)$$
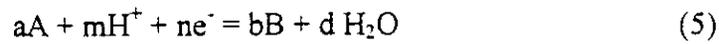
half-cell potentials can be calculated by using [31]:

$$e = e^o - 0.059\ (m/n)\ pH + (0.059/n)\ log\ [(A)^a/(B)^b] \quad (6)$$

Reactions (2) and (4) require the activity of [B] as partial pressure of hydrogen gas and reaction (3) requires the activity of [A] as the partial pressure of oxygen gas, to determine the half-cell potentials by equation (6).

The pressure may be calculated as approx. 9 to 30 atm. at water depths of 300 to 1000 ft., respectively. Using these pressure values for hydrogen and oxygen gases in deep-water, an expansion of water stability region is indicated on the Pourbaix's Diagram (Figure 9). The water stability region is expanded by 40 and 130 mV for gas pressures of 9 and 30 atm., respectively. Thus, it should be appreciated that a variation in temperature, pressure and ionic activities can influence the possibility of corrosion in deep-water.

Corrosion Protection

Three approaches are essentially available to combat corrosion in deep-sea environment. In addition to proper **material selection** described in this paper, **cathodic protection** may be applied in combination with **non-metallic organic coatings**. Cathodic protection with impressed current, as well as sacrificial anode can be used. Anodic protection is not effective in sea-water.

In the sacrificial anode mode, three galvanic anodes are used in marine cathodic protection technology. Zn, Al and Mg alloys are employed with careful control of composition and thermal history. Excessive corrosion of sacrificial anodes is prevented by properly selecting alloys. Alakline solution is produced adjacent to the cathodes (surface being protected) due to the (i) consumption of H^+ (reaction 2) or production of OH^- ions (reactions 3 & 4). This high alkalinity can corrode amphoteric metals such as Al, Pb or Zn. Excessive evolution of hydrogen (reactions 2 & 4) gas can also affect non-metallic organic coatings such as paints.

Impressed current cathodic protection is more common in deep-sea environment due to the ease of application. Typically, cathodic protection, in both the forms, is used as a back-up to organic coatings. 5mA/ft^2 current-density is required to protect bare steel in quiet seawater. Zn can deliver 350 A-hr/lb. Thus, 100 ft^2 of steel can be protected by a 12 lb zinc anode for 14 months [33]. Cathodic protection current is lowered by paints and the paint is protected by creeping damage if current is not excessive. A good vinyl paint can lower the current requirement five-folds. Aluminum alloy can have slightly more active potential with an output of 1000 A-hr/lb. Organic coatings are used, therefore, to minimize the current requirements in the impressed current mode or the quantity of metal in the sacrificial mode.

It is difficult to maintain 100 % integrity in any coating. Metals with noble solution potentials cause intensified attack of active unalloyed steel or aluminum due to the difference in

potentials and unfavorable relative areas of anode and cathode. Pin-holes and holidays in the coatings negatively influence the relative areas, causing the active metals to corrode faster. Inert metallic coatings are, therefore, ineffective. Zinc or aluminum active metal coating is useful to protect steel galvanically. If these metals are used to protect the structural alloys beneath a non-metallic coating at coating defects, cathodic protection is effective and inexpensive.

Prominent non-metallic coatings are **Anti-fouling coatings,** that prevent settlement of fouling spores and organisms by continuous release of toxic substances, and **Self-polishing copolymers** [SPC], that incorporate toxins in matrix which are sparingly soluble in sea-water. Thus, fresh paint/water interface is continuously generated. It should be emphasized that in these systems some form of erosion is required for sufficient dissolution of toxins. Additionally, **silicone-rubber-based** materials are also used as coatings, such as, polydimethylsiloxanes. Typical toxins used for deep-water protection are cuprous oxide and tributyl tin oxide. Fouling is prevented by a release of $10\mu g/cm^2/day$ of toxins. For deep ocean structures, a 0.012-0.015 in. organic barrier coating is used [34].

Stainless steel has excellent corrosion resistance in deep-sea environment. Cladding of less expensive metals and alloys by stainless steel is viable option. However, there is a cut-off where cladding is less effective than application of a paint (Figure 10). Additional protection of concrete structures is realized by **encasement** of concrete using bitumastic coatings, bagged and sacked concrete, metallic sheathing, epoxy resins and gunite.

Figure 10: Comparison of stainless cladding and paint repair as a function of life.

Hydrogen embrittlement

High strength welded structures are particularly susceptible to hydrogen damage. Table I shows the amount of total hydrogen present in a medium-carbon high-strength steel. It should be noted that it is only the diffusible hydrogen that is damaging to the steel. There are several sources of hydrogen in deep-sea environment. Use of cathodic polarization to prevent corrosion of steel in underwater service influences the hydrogen ion discharge on the metal surface. However, the sensitivity of a particular steel to embrittlement is dependent on amount of hydrogen entering the steel and the operative stress system. Hydrogen damage is dependent on the loading condition, where a static tensile load is typically required for hydrogen cracking of steel. Depending on the structure, the hydrostatic pressure could load the structure in tension, compression or both. Embrittlement is not caused under protective potentials of around -0.8 V vs. SCE. However, the role of over-protection, high hardness regions and sulfate reducing bacterial interaction by anaerobic growth (SRB) could give rise to embrittlement. The role of microbial reactions on generation of hydrogen sulfide is shown in Figure 11 [35].

Table I: Total hydrogen content of steel under different corrosion conditions

Figure 11: Generation of H_2S gas by anaerobic bacterial growth

Materials Performance in the Deep Ocean

Many materials perform significantly different in the deep ocean than they do in near-surface waters. As will be shown below, this difference in performance may result in either greater amounts of corrosion at depth or less, depending on the alloy. In general, the differences in corrosion behavior can be related to oxygen content, although as has been shown above, the differences are due to the combined effects of many variables. The deep ocean corrosion behavior reported here is primarily drawn from the pioneering efforts of Fred M. Reinhart who began deep ocean corrosion testing in the 1960's and provided much guidance to one of the authors (Jenkins) in developing a knowledge of marine corrosion.

Aluminum alloys depend on an oxide film for their corrosion resistance. Reduced oxygen contents and reduced pH in mid depth waters results in an acceleration of pitting damage on many aluminum alloys including one of the most common alloys, 6061-T6. As shown in Figure 12, the profile of pitting depths during one year of exposure varies with depth in a manner reverse to the curves for oxygen content and pH. [36]. This data can be replotted to show the variation of the pit depths with oxygen content rather than with depth as in Figure 13.
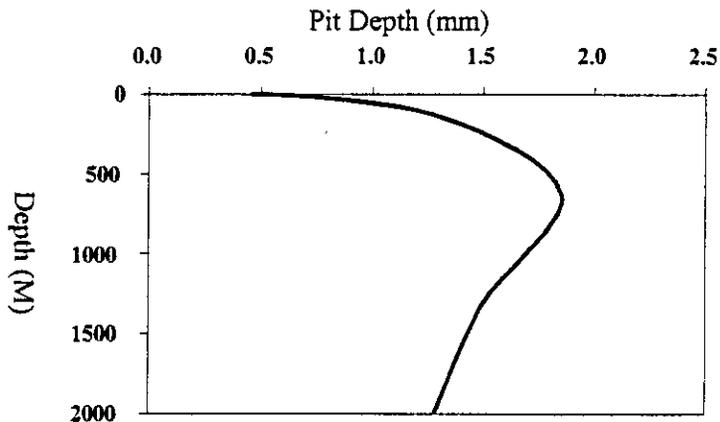
Figure 12. Profile of maximum pit depths with depth (Al alloy 6061-T6) one year of exposure.

Copper alloys are little affected by variations in environment with depth. Their corrosion rates remain low, in the range of 0.125 – 0.5 mm/y (0.5 to 2.0 mpy) [37].

Nickel alloys are similarly unaffected by the variation in environment with depth. Alloys that are susceptible to corrosion (primarily crevice corrosion) remain susceptible at depth and those resistant to corrosion in near-surface environments remain resistant at depth. [38]

Stainless steels show a minimal effect of depth on performance. In some cases there appears to be some reduction in the propagation rates for crevice corrosion, but the conditions required to initiate crevice corrosion on the stainless steels appear to be unaffected by variations in environment with depth [39].

Steels show a dramatic variation of corrosion with depth. Their performance can be directly related to the oxygen content of the seawater as shown in Figure 14 for low carbon steel (1020) [40]. Other carbon steels, alloy steels and cast irons showed similar behavior [41].
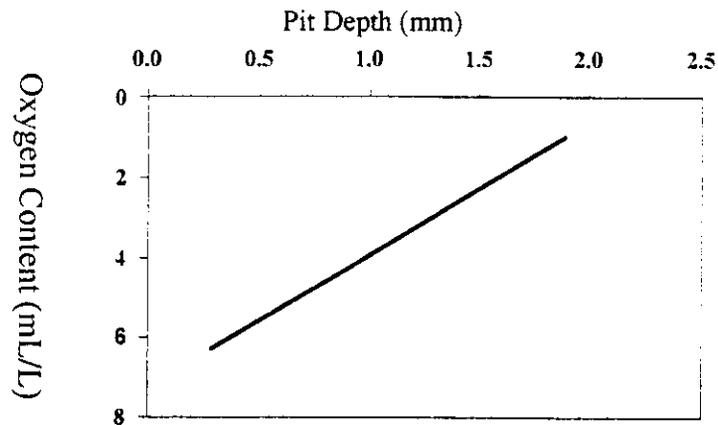

Figure 13. Variation in pit depth with O_2 content (Al alloy 6061-T6) one year of exposure.
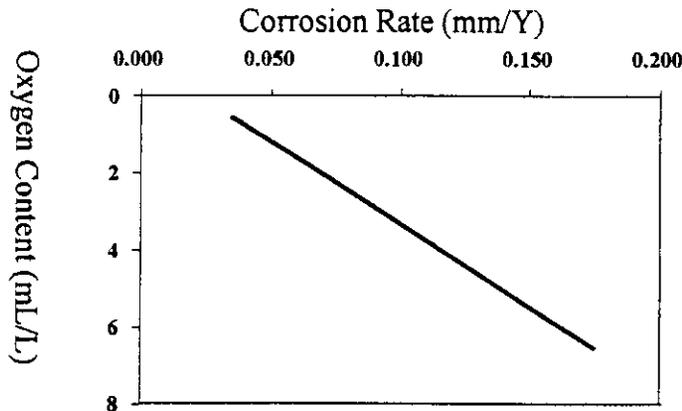
Figure 14. Variation in corrosion rate with oxygen content (carbon steel) one year of exposure.

Titanium alloys showed no pitting, crevice or uniform corrosion in any of the deep ocean corrosion tests [42]. Some highly susceptible alloys showed susceptibility to stress corrosion cracking in the static loaded and ring welded specimens used to evaluate stress corrosion cracking. However, there was no clear affect of depth on stress corrosion cracking [43]. Other than natural notches associated with the welding of the specimens, no notches were present.

Miscellaneous alloys such as lead, tin and a cobalt-based superalloy showed little or no affect of depth on performance [44]. Other alloys such as zinc shoed an increase of corrosion rate with increasing oxygen content [45].

Non-metallic materials are affected by exposure to both shallow and deep-water environments. Biological activity is the primary cause of this deterioration with the organisms either metabolizing the materials directly or damaging the material when they seek shelter. In the deep ocean, this activity is slowed compared to shallower environments, but remains

significant. Attack is significantly enhanced when the non-metallic materials are in contact with materials such as wood that serve as bait for the initial infestation and growth of boring organisms. [46-50].

Glasses and ceramics may be used under compressive loading in deep-water from the strength point of view. Ceramics are mostly resistant to corrosion in near neutral or slightly alkaline pH.Plastics (polymers), such as the thermoplastic acrylics (plexiglass) are used as view ports on deep-sea vehicles. Non-metallics have low strength unless they are metal-reinforced. Fiber reinforced polyester resin show deterioration in matrix strength in sea-water. Wood as structural member, is limited by the fact that fatigue strength is at 27 % of rupture modulus after 10^6 cycles and that wet wood working stress parallel to the grain in compression is at 90% of the dry condition and only 70 % in normal direction.

Need for Further Research

As man increases his exploitation of the world's oceans, his activities are certain to take him to even deeper depths. This venture will require additional knowledge of the effects of the deep ocean environment on materials. Many new materials have been developed since the majority of deep ocean corrosion testing was completed in the 1970's. The performance of entire classes of materials, such as the duplex stainless steels and the superaustenitic stainless steels in the deep ocean has not been evaluated. There is a need for evaluating m the deep-ocean corrosion behavior materials that have shown good corrosion resistance in near surface waters. One method for evaluating the performance of materials in deep ocean environments is to evaluate the condition of objects that are either intentionally or inadvertently exposed to the deep ocean. This requires a systematic evaluation of the objects immediately upon recovery by qualified corrosion personnel. The methods for these systematic evaluations have been developed and documented [51-56].

While the performance of coatings in deep ocean environments has been evaluated and found do differ significantly form deterioration of coatings in near-surface environment [57], many newly developed coatings have not been evaluated in the deep ocean.

Hydrogen embrittlement is a concern with many of the high strength materials that would otherwise be good candidates for use in deep ocean systems. The hydrogen embrittlement resistance of many alloys has been assessed in tests under laboratory conditions and limited testing in near-surface waters. However, primarily due to the difficulty of performing these for hydrogen embrittlement in remote locations, little, if any testing of hydrogen embrittlement resistance in the deep ocean has been performed. This is of particular concern as two factors that are known to affect hydrogen embrittlement, pressure and pH are known to vary with depth in a manner that should enhance hydrogen embrittlement at some deep ocean sites [58].

Summary

The deep ocean environment is sufficiently different from the ocean environment near the surface to result in significant variations in material performance between the two environments. Some deep ocean materials testing has demonstrated these differences and generated a limited

capability to predict materials behavior at depth. However, for optimum design of deep ocean structures and equipment, much more information must be generated.

References

1. Allmendinger, E. Eugene, ed., "Submersible Vehicle Systems Design", The Society of Naval Architects and Marine Engineers, 1990, pp.52-54.
2. Sverdrup, Johnson & Fleming, "The Oceans", Prentice-Hall, Inc. 1970, pp. 71,72.
3. "Shrier, L.L. "Corrosion", Volume 1. Butterworth - Hinemann, 1994, p.2: 66.
4. NACE International, "Corrosion Control of Steel Fixed Offshore Platforms Associated with Petroleum Production", Recommended Practice RP0176-94, 1194, p.29.
5. LaQue, F.L. "Marine Corrosion- Causes & Prevention", John Wiley & Sons, 1975, p.116.
6. Ibid.
7. La Que, Op. Cit, p 14.
8. "Ibid."
9. Shrier, Op.Cit., p. 3:16
10. Hasson, D.F. & Crowe, C.R., "Materials for Marine Structures and Systems", Academic Press, Inc, 1988, p.186.
11. La Que, Op.Cit., pp. 104 – 110.
12. Dexter, S.C. "ASM Handbook, Volume 13 - Corrosion", ASM International, 1996, p.897.
13. Shrier, Op.Cit., p. 2:64.
14. Sverdrup, Johnson & Fleming, Op.Cit., p. 198.
15. Compton, K.G, "The Unique Environment of Seawater and Its Effect on Corrosion of Metals", Corrosion Journal, NACE International, October 1970, p. 448 ff.
16. Dexter, S.C. "ASM Handbook, Volume 13 - Corrosion", ASM International, 1996, p.901.
17. Hasson, D.F. & Crowe, C.R., Op.Cit., p.132.
18. Hasson, D.F. & Crowe, C.R., Op.Cit., p.204
19. Hasson, D.F. & Crowe, C.R., Op.Cit., p.170
20. Sverdrup, Johnson & Fleming, Op.Cit., p. 776.
21. Ibid.
22. Ibid.
23. Dexter, S.C. "ASM Handbook, Volume 13-Corrosion", ASM Intl., 1996, pp. 895-900.
24. J. A. Beavers, et. al., "Corrosion of Metals in Marine Environments", Battelle Columbus Division, Columbus Ohio, July 1986, p.1-23.
25. Dexter, S.C. "ASM Handbook, Volume 13 - Corrosion", ASM International, 1996, p. 897.
26. Sverdrup, Johnson & Fleming, "The Oceans", Prentice-Hall, Inc. 1970, p749.
27. Reinhart, F.M, "Corrosion of Metals and Alloys in the Deep Ocean – Technical Report R 834", Civil Engineering Laboratory, Port Hueneme, California, February 1976, p. 4.
28. Sverdrup, Johnson & Fleming, "The Oceans", Prentice-Hall, Inc. 1970, p805.
29. Sverdrup, Johnson & Fleming, "Op.Cit., pp. 807, 808.
30. Allmendinger, E. Eugene, ed., "Submersible Vehicle Systems Design", The Society of Naval Architects and Marine Engineers, 1990, p. 80.
31. Jones, D.A., "Principles and Prevention of Corrosion", 2nd Edition, Prentice-Hall, Inc., N.J., 1996, p. 61
32. Al_Hassan, S.J., "Environmental and Microstructural Effects on Corrosion of Linepipe Steels in CO_2-containing Solutions", Ph.D. Thesis, No. T-4598, Colorado School of Mines, 1994.

33. Gaythwaite, J., "The Marine Environment and Structural Design", Van Nostrand Reinhold Co., NY, 1981, p. 289.
34. Myers, J.J., et.al., ed., "Handbook of Ocean and Underwater Engineering", McGraw-Hill Co., NY, 1969, p. 7-52.
35. Lewis, J.R. and Mercer, A.D. ed, "Corrosion and Marine Growth on Offshore Structures", Soc. Of Che,m. Ind., 1984, p. 121.
36. Reinhart, F.M, "Corrosion of Metals and Alloys in the Deep Ocean – Technical Report R 834", Civil Engineering Laboratory, Port Hueneme, California, February 1976, pp.213-214.
37. Reinhart, Op.Cit, pp 43-88.
38. Reinhart, Op.Cit, pp 89-127.
39. Reinhart, Op.Cit, pp 129-184.
40. Reinhart, Op.Cit, pp 7-42.
41. Ibid.
42. Reinhart, Op.Cit, pp 225-238.
43. Ibid.
44. Reinhart, Op.Cit, pp 239-251.
45. Ibid.
46. Muraoka, J.S., "Deep Ocean Biodeterioration of Materials, Part II, Six Months at 2340 Feet", Naval Civil Engineering Laboratory Technical Report R393, 1965.
47. Muraoka, J.S., "Deep Ocean Biodeterioration of Materials, Part IV, One Year at 6800 Feet", Naval Civil Engineering Laboratory Technical Report R456, 1966.
48. Muraoka, J.S., "Deep Ocean Biodeterioration of Materials, Part V, Two Years at 5640 Feet", Naval Civil Engineering Laboratory Technical Report R495, 1966.
49. Muraoka, J.S., "Deep Ocean Biodeterioration of Materials, Part VI, One Year at 2370 Feet", Naval Civil Engineering Laboratory Technical Report R525, 1967.
50. Muraoka, J.S., "Deep Ocean Biodeterioration of Materials – Six Months at 6000 Feet", Naval Civil Engineering Laboratory Technical Note N-1081, 1970.
51. Jenkins, J.F., "Inspections of Objects Recovered from the Deep Ocean – AUTEC Acoustic Array, NCEL Technical Note N -1424, February 1976.
52. Jenkins, J. F., "Corrosion Analysis of St. Croix Underwater Tracking Arrays", CEL Technical Note N -1500, September 1977.
53. J. F. McCartney, J.P. Sandlin, J. F. Jenkins, J.S. Muraoka, D.G. True, "Recovery, Inspection and Analysis of World War II Aircraft After 26 Years at 560 Fathoms", NCEL Technical Memorandum 43-71-3, March 1971.
54. J. F. Jenkins, "Analysis of the Condition of the SNAP 7-E Acoustic beacon Installation After 64 Months at 2,650 Fathoms", NCEL Technical Note N -1192, February 1972.
55. J. F. Jenkins, "Analysis of Hydrophone Support Structure After 52 ½ Months Exposure at a Depth of 5270 feet in the Barking Sands Test Range, Kauai, Hawaii", J. F. Jenkins, NCEL Technical Note N -1267, March 1973.
56. J. F. Jenkins, "Analysis of the Condition of ECHO Tower, Azores Fixed Acoustic Range After One Year at 1500 Feet of Depth", NCEL Technical Note N -1284, May 1973.
57. Rynewicz, J. F., "Evaluation of paint coatings tested in the deep Atlantic and Pacific oceans", in American Society for Testing and Materials STP 558 "Corrosion in Natural Environments", 1973, pp 231-234.
58. Shrier, Op.Cit., p. 8:92-95.

Risk and Reliability Analysis of Corrosion of Marine Pipelines

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ABSTRACT

This paper addresses application of qualitative and quantitative analytical methods in the risk assessment and management of marine pipeline sytems for corrosion. Both qualitative and quantitative analytical methods have found widespread use in risk assessment and management of pipelines (Muhlbauer 1992; Kirkwood, Karam, 1994; Kulkarni, 1994; Nessim, Stephens, 1995; Collberg, Cramer, Bjornoy 1996; Office of Pipeline Safety, 1997; Zimmerman, et al 1998; Bai, Song, 1998).

This paper proposes a general engineering approach for risk assessment and management of marine pipeline systems subjected to corrosion (RAM PIPE) The approach is based on use of qualitative, quantitative, and mixed qualitative – quantitative analytical methods. This paper will outline the approach, its attributes and strategies, and further develop the qualitative – quantitative approach for design and reassessment of pipelines subjected to corrosion.

RAM PIPE APPROACH

The fundamental steps of the RAM PIPE approach are identified in Figure 1. The steps may be summarized as follows:

1) **Identification** – this selection is based on an assessment of the likelihood of finding significant degradation in the quality (serviceability, safety, durability, compatibility) characteristics of a given pipeline system, and on an evaluation of the consequences that could be associated with the degradation in quality. The selection can be triggered by either a regulatory requirement or by an owner's initiative, following an unusual event, an accident, proposed upgrading of the operations, or a desire to significantly extend the life of the pipeline system beyond that originally intended.

2) **Condition survey** – this survey includes the formation of or continuance of a databank that contains all pertinent information the design, construction, operation, and maintenance of a pipeline system. Of particular importance are identification and recording of exceptional events or developments during the pipeline system history. Causes of damage or defects can

START

Select
Asses &
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Procedure
to
qualify

Evaluate
of
Results

LEVEL
Scoring
Quali...

1 LEVEL
Simplified
Mix...

2 LEVEL
Quantitative
Analysis

Next
Engineering
Inspection
Maintenance
Repair

Re-Evaluate
Pipeline
Loading
& Protection
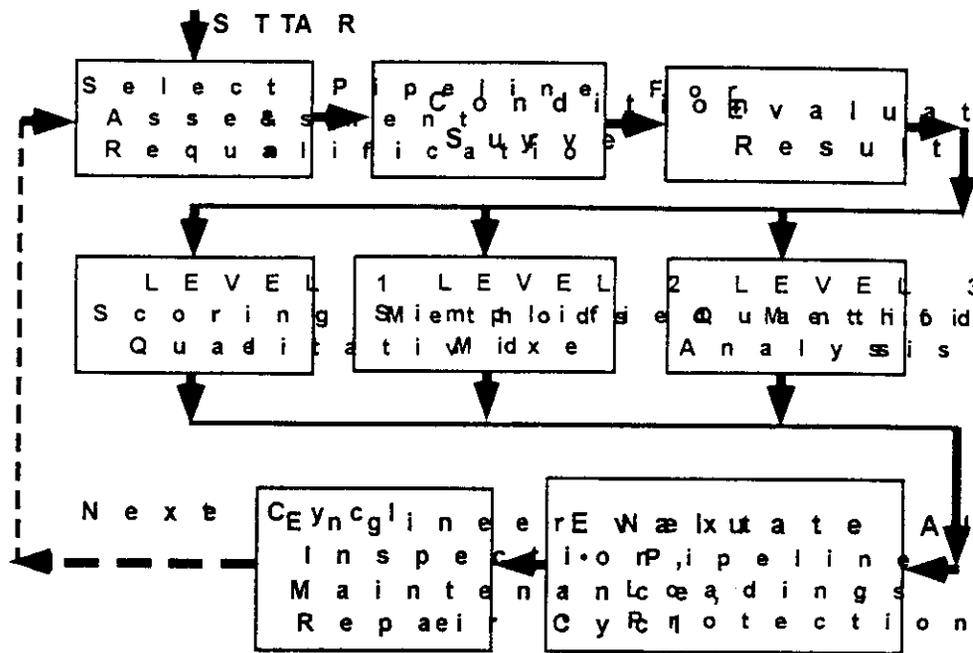
Figure 1 – RAM PIPE Approach

provide important clues in determining what, where, how ,and when to inspect and/or instrument the pipeline system. This step is of critical importance because the RAM PIPE process can only be as effective as the information that is provided for the subsequent evaluations (garbage in, garbage out).

3) **Results assessment** – this effort is one of assessing or screening the pipeline system based on the presence or absence of any significant signs of degradation its quality characteristics. The defects can be those of design, construction, operations, or maintenance. If there appear to be no potentially significant defects, the procedure becomes concerned with engineering the next IMR cycle. If there appear to be potentially significant defects, the next step is to determine if mitigation of these defects is warranted. Three levels of assessment of increasing detail and difficulty are proposed: Level 1 – Qualitative (Scoring, Muhlbauer 1992; Kirkwood, Karam 1994), Level 2 – Simplified Qualitative – Quantitative (Bea, 1998), and Level 3 – Quantitative (Quantitative Risk Assessment, QRA, Nessim, Stephens 1995; Bai, Song 1998; Collberg, et al 1996).

The basis for selection of one these levels is one that is intended to allow assessment of the pipeline with the simplest method. The level of assessment is intended to identify pipelines that are clearly fit for purpose as quickly and easily as is possible, and reserve more complex and intense analyses for those pipelines that warrant such evaluations. The engineer is able to choose the method that will facilitate and expedite the requalification process. There are more stringent Fitness for Purpose (FFP) criteria associated with the simpler methods because of the greater uncertainties associated with these methods, and because of the need to minimize the likelihood of 'false positives' (pipelines identified to FFP that are not FFP).

4) **Mitigation measures evaluation** – mitigation of defects refers to prioritizing the defects to remedied (first things first), and identifying practical alternative remedial actions. The need

for the remedial actions depends on the hazard potential of a given pipeline system, i.e., the likelihood that the pipeline system would not perform adequately during the next RAM PIPE cycle. If mitigation appears to be warranted, the next step is to evaluate the alternatives for mitigation.

5) **Evaluating alternatives** – mitigation alternatives include those concerning the pipeline itself (patches, replacement of sections), its loadings (cover protection, tie-downs), supports, its operations (pressure de-rating, pressure controls, dehydration) maintenance (cathodic protection, corrosion inhibitors), protective measures (structures, procedures, personnel), and its information (instrumentation, data gathering). Economics based methods (Kulkarni, Conroy 1994; Nessim, Stephens 1995), historic precedents (data on the rates of compromises in pipeline quality), and current standards of practice (pipeline design codes and guidelines, and reassessment outcomes that represent decisions on acceptable pipeline quality) should be used as complimentary methods to evaluate the alternatives and the pipeline FFP. An important alternative is that of improving information and data on the pipeline system (information on the internal characteristics of the pipeline with instrumentation – 'smart pigs' and with sampling, information on the external characteristics of the pipeline using remote sensing methods and on-site inspections).

6) **Implementing Alternatives** – once the desirable mitigation alternative has been defined, the next step is to engineer that alternative and implement it. The results of this implementation should be incorporated into the pipeline system condition survey – inspection databank. The experiences associated with implementation of a given IMR program provide important feed-back to the RAM PIPE process.

7) **Engineering the next RAM PIPE cycle** – the final step concluding a RAM PIPE cycle is that of engineering and implementing the next IMR cycle. The length of the cycle will depend on the anticipated performance of the pipeline system, and the need for and benefits of improving knowledge, information and data on the pipeline condition and performance characteristics.

LEVEL 2 ASSESSMENT OF BURST CAPACITY OF CORRODED PIPELINES

Formulation

To illustrate application of the foregoing developments, a Level 2 simplified qualitative – quantitative analysis approach will be utilized to evaluate in-place wall thickness requirements for pressure containment - burst capacity of a pipeline. In this approach, pipeline strength was formulated in terms of the capacity of the pipeline to withstand the imposed pressures (internal, external) without loss of containment (rupture). The strength was formulated as (DNV, 1996; ISO, 1996; BSI, 1993; API, 1993; Bai, et al, 1994; 1997; Sotberg et al, 1997; ASME 1991):

$$t / D = p / 2 S$$

where t is the existing minimum thickness of the pipeline, D is the diameter of the pipeline, p is the maximum net pressure (internal - external) that the pipeline must be capable of containing, and S is the ultimate strength of the steel in the pipeline.

The API guidelines (1993) specify burst strength as:

$$t / D = (p / 2 \text{ Sym } f)$$

where Sym is the specified minimum yield strength of the pipeline steel. The term 'f' represents the product of three terms: fd (design factor), fe (weld joint factor), and ft (temperature de-rating factor). The design factor is 0.72 for liquid and gas pipelines, 0.60 for liquid pipelines and risers on platforms, and 0.50 for gas pipelines and risers on platforms. The weld joint factor is specified as generally being 1.0 (when welding is conducted according to the specified codes and guidelines). The temperature de-rating factor is used for high temperature pipelines and the de-rating is specified by ASME guidelines (ASME B31.4 and ASME B31.8) (ASME, 1991). The 'f' factor can be interpreted as a factor-of-safety (FS = f^1).

In the API guidelines, t is the nominal or design wall thickness of the pipeline or riser. The guidelines specify a number of measures that should be used to prevent corrosion or loss of wall thickness both inside and outside the pipeline or riser. Thus, this guideline is based on the assumption that the pipeline or riser operator will provide and maintain the pipeline so that little or no corrosion takes place. A corrosion allowance or thickness could be provided to recognize the need to allow some corrosion to take place without having to de-rate or replace the pipeline. This corrosion allowance is not specified in the API guidelines.

The DNV guidelines (DNV, 1996; Sotberg et al, 1996; Jiao, et al, 1997; Bai, et al, 1994; 1997) specify burst strength as:

$$t / (D-t) = p / (2 . 1.1 . S \cdot \eta_u)$$

where η_u is a usage factor that depends on the safety class of the pipeline or riser. For a High Safety Class, $\eta_u = 0.67$. For a Normal Safety Class, $\eta_u = 0.70$. For a Low Safety Class, $\eta_u = 0.74$. Given the 1.1 that is multiplied times S, these values are very close to those of API.

However, in this case, the 't' that is referenced is the net wall thickness after corrosion has taken place. Corrosion protection can be provided to make this 't' the same as is referenced in API. However, if no protection is provided, a corrosion allowance must be estimated and added to the nominal wall thickness of the pipeline or riser to define the design wall thickness.

A RAM based formulation of the foregoing developments can be developed as follows presuming that the demand (operating pressure) and capacity (pipeline burst pressure) are Lognormally distributed variables:

$$p_B = 2 S t / D$$

where p_B is the pipeline burst pressure, S is the stress associated with the burst strength of the pipeline, t is the pipeline wall thickness, and D is the pipeline diameter.

$$Pf = P (p_O \geq p_B)$$

where Pf is the probability of failure, p_O is the maximum operating pressure, and P (X) is read as the probability of (X).

$$Pf = 1 - \Phi\{ [\ln (p_{B50} / p_{O50})] / [(\sigma^2_{pB} + \sigma^2_{pO})^{0.5}]\}$$

where Φ is the standard cumulative Normal distribution, p_{B50} is the 50th percentile (median) burst pressure, p_{O50} is the 50th percentile maximum operating pressure, σ_{pB} is the standard

deviation of the logarithms of the burst pressure, and σ_{pO} is the standard deviation of the logarithms of the maximum operating pressures.

$$\beta = \ln (p_{B50} / p_{O50}) / \sigma = \ln FS_{pB/O\ 50} / \sigma$$

β is the Safety Index, $FS_{pB/O\ 50}$ is the central or median Factor of Safety between the pipeline burst pressure and the maximum operating pressure, and σ is the total uncertainty in the pipeline burst pressure and operating pressure.

$$p_B = p_O (B_{pO} / B_{pB}) \exp (\beta \sigma) = p_O B \exp (\beta \sigma)$$

p_B is the 'nominal' burst pressure, p_O is the 'nominal' maximum operating pressure, B_{pO} is the median 'bias' in the nominal burst pressure, B_{pB} is the median bias in the nominal maximum operating pressure, and B is the resultant median bias in the nominal burst and operating pressures. Bias is defined as the ratio of the true value to the nominal (predicted, calculated) value. It is to be noted that for the premises of this development (Lognormally distributed independent demands and capacities) that this is an 'exact' expression.

A non-dimensional pipeline wall thickness to diameter ratio can be expressed as:

$$t / D = (p_O / 2 S) (B \exp (\beta \sigma_{\ln p/R}))$$

In this development, the Bias in the demand is taken as Bp = 1.0. This bias presumes that on the average that the pipeline will be operated at the design maximum operating pressure.

The Bias in the capacity was taken as B_R = 2.0. This bias is based on comparisons of pipeline burst strength tests compared with the burst strengths predicted by the hoop stress formulation used in this development (B_R = 1.7, Figure 2) (Bai, et al, 1994; Bai, Xu, Bea, 1997), and the strength of the steel at which the pipeline ruptures or looses containment (B_R = 1.2) (Jiao, et al, 1997). σ is the total Type 1 (natural, inherent) uncertainty in the demand and capacity elements:

$$\sigma^2_{\ln p/R} = \sigma^2_{\ln p} + \sigma^2_{\ln R}$$

The uncertainty in the demand was evaluated to be $\sigma_{\ln p}$ = 0.10. This variability represents the natural or inherent variability in the pipeline or riser operating pressures (Bai, Xu, Bea, 1997; Sotberg, Leira, 1994). The uncertainty in the capacity was evaluated to be $\sigma_{\ln R}$ = 0.20. This uncertainty represents the natural or inherent variability in the pipeline burst capacity as influenced by the variability in steel and welding strength (pipeline strength), steel thickness, pipeline or riser diameter, and corrosion thickness. The total or resultant uncertainty was thus evaluated to be $\sigma_{\ln p/R}$ = 0.22.
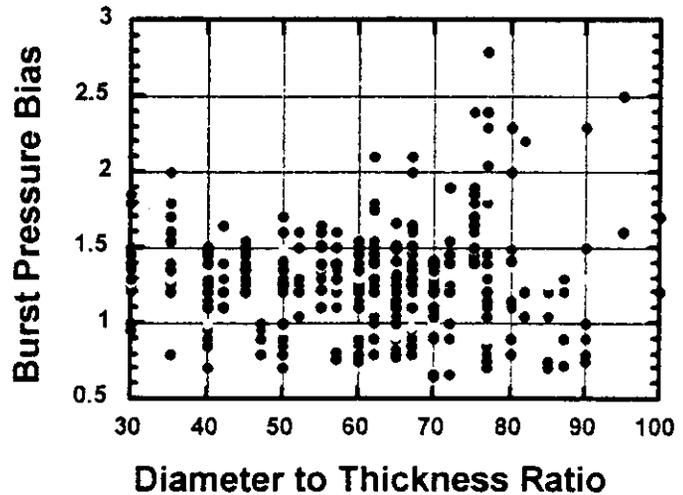

Figure 2 - Comparison of predicted and test burst pressures for pipelines with varying diameter to thickness ratios

Note that this resultant uncertainty has not taken into account the variability added by corrosion damage or defects in the pipeline. Because corrosion has a very high natural variability and the effect of this variability on the burst capacity is also high, the total or resultant uncertainty for a moderately corroded pipeline based on the burst capacity formulation used here could increase to $\sigma_{lnp/R} = 0.40$ to 0.50. For severely corroded pipelines, $\sigma_{lnp/R} = 0.60$ to 0.80.

The Safety Index (measure of reliability) could be expressed as:

$$\beta = \ln \left[(2 \, B \, S / p_O \, D) \, (t - t_{ci/e}) \right] / \sigma_{lnp/R}$$

The reliability based dimensionless ratio of pipeline or riser wall thickness to diameter (t / D) exclusive of corrosion thickness allowances can thus be expressed as:

$$t / D = (p_O / 2 \, S \,) \, [B \exp (\beta \, \sigma_{\,lnp/R})]$$

$$t / D = (p_O / S) \, [(1.0 / 2.0 \cdot 2) \exp (\beta \, 0.22)]$$

$$t / D = p_O / S \, (0.25 \exp 0.22 \, \beta)$$

This formulation allows the dimensionless thickness to diameter ratio of the pipeline or riser (t/D) to be expressed as a function of the dimensionless ratio of the expected maximum operating pressure to specified minimum steel yield strength (p / S) times the exponential of 0.22 times the annual Safety Index (β). The t / D ratio is graphed as functions of p_O / S and β in Figure 3 for the total uncertainty of 22 %.

For a given maximum operating pressure to specified minimum yield strength ratio (p/S), for the lower p/S ranges there are small differences between the t / D ratios for new and existing pipelines. There are relatively insignificant differences between the different pipeline Serviceability and Safety Classes. Significant differences show up only for the higher operating pressure to yield strength ratios. Note that the differences between new and existing pipelines shown in Figure 12 do not incorporate the larger uncertainties associated with existing corroded pipelines.

Figure 4 shows the results for a total uncertainty of 40%. There is dramatic increase in the required t/D ratios for given ratios of operating pressure to yield strength. In this case, the wall thickness that are referenced are those after corrosion; i.e. they are the minimum wall thickness in a given segment of a pipeline. The increase in required t/D ratios is one of the prices of allowing significant corrosion to develop inside or outside of a pipeline.
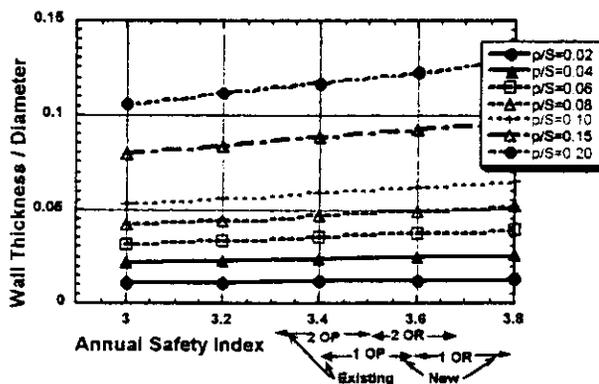

Figure 3 - Thickness to diameter ratio as function of ratio of maximum operating pressure to steel yield strength and annual Safety Index for total uncertainty of 22%
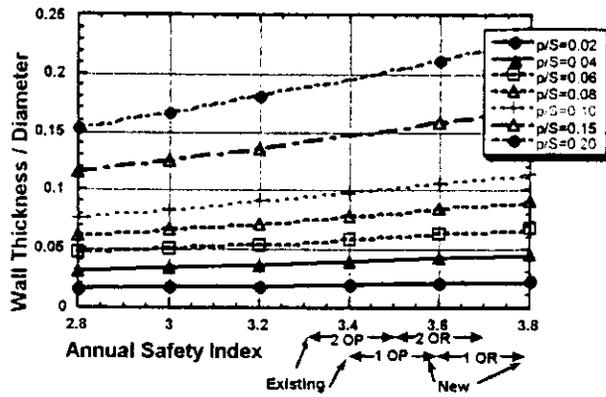
Figure 4 - Thickness to diameter ratio as function of ratio of maximum operating pressure to steel yield strength and annual Safety Index for total uncertainty of 40%

API Guideline Based Design Factors

The foregoing could be cast in the same form as the API guidelines as follows. Based on the RAM formulation:

$$t / D = (p_O / 2 S) (B \exp (\beta \sigma_{lnp/R}))$$

$$p_O = (2 S t / D) (B \exp (\beta \sigma_{lnp/R}))^{-1}$$

Based on the API guidelines:

$$t / D = (p_O / 2 S f)$$

$$p_O = (2 S t / D) (f)$$

Thus,

$$f = (B \exp (\beta \sigma_{lnp/R}))^{-1}$$

The API based risk assessment and management formulation for the design factor 'f' is summarized in Figure 5. Also shown are the API design factor guidelines for liquid and gas pipelines and platform risers. For the uncertainties associated with new or uncorroded pipelines, the API guidelines result in very high reliability pipelines. However, the performance history of pipelines in the Gulf of Mexico for corrosion failures indicates corrosion failures of 'typical' pipelines at the rate of 2 E-2 to 5 E-2 per year (Mandke, 1990; Mandke, et al, 1995; marine Board, 1994; Elsayed, Bea, 1997). This is equivalent to annual Safety Indices in the range of β = 1.5 to 2. This Safety Index range is commensurate with the uncertainties associated with corroded pipelines. The analytical models indicate probabilities of failure that agree well with the performance history.

The annual Safety Indices associated with the API design factors could be determined from:

$$\beta = \ln (1/f B) / \sigma_{lnp/R}$$
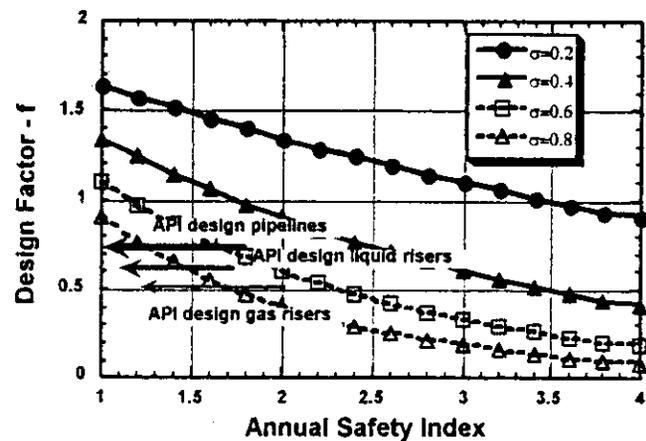
Figure 5 - API burst pressure design factor

Given this development, and an assessment of a total uncertainty of 50% for API pipeline design (allowing for corrosion uncertainties), a median bias in the pipeline demand and capacity of B = 2.0, one could determine the annual Safety Index for pipeline design implied by the API guidelines as β = 2.0 (Pf ≈ 1 E-2 per year) for subsea oil and gas pipelines, β = 2.4 for oil risers, and β = 2.8 for gas risers. These values are in excellent agreement with the performance characteristics of pipelines and risers in the Gulf of Mexico (Pf ≈ 1 E-2 per year).

Corrosion – Un-Instrumented Pipelines

Experience with Gulf of Mexico pipelines and risers (oil and gas) has clearly shown that the primary operating hazard to the integrity of pipelines and risers is corrosion; primarily internal corrosion for pipelines, and external corrosion for risers (generally in the vicinity of the mean water level) (Elsayed, Bea, 1997; Marine Board, 1994; AME 1993; Mandake, 1990).

For un-instrumented pipelines, a combination of subjective judgement and database information from instrumented and un-instrumented pipeline performance must be used to evaluate corrosion. Figure 6 summarizes the causes of pipeline failures in the OCS waters of the Gulf of Mexico during the period 1980 through 1996. This summary includes 2,332 failures for 10,553 pipelines. Failure is defined as a loss of containment resulting in a substantial loss of hydrocarbons from the pipeline or riser). The primary cause of failure is corrosion; about 50 % of the failures are due to corrosion. Hurricanes (natural hazards) are responsible for about 25 % of the failures. The remaining 25 % of the failures can be attributed to Human and Organizational Factors (HOF) (Bea, 1994).

Based on the same database, Figures 7 and 8 shows the causes of pipeline failures for oil and gas pipelines, respectively. The distribution of the causes of failures is about the same for both oil and gas pipelines. Corrosion again accounts for about half of the failures. Most surprising was the large proportion of gas pipelines that fail due to corrosion. Improvements in gas dehydration could help reduce this source of failures.

The database contains information on the distribution of failures caused by external and internal corrosion. As summarized in Figure 9, in the case of risers, external corrosion accounts for about 85 % of the corrosion related failures. The vast majority of this corrosion is located at and above the mean sea level. In the case of submerged pipelines, internal corrosion accounts for about 75 % of the corrosion related failures The database did not indicate any significant differences between the failure rates for small and large diameter pipelines.

Figure 10 shows the distribution of times to corrosion failures for gas pipelines. The data includes gas pipelines with and without gas dehydration. The mean time to failure is about 10 years. The Coefficient of Variation (ratio of standard deviation to mean, COV) of the time to failure is about COV ≈ 100 %. This very large COV is due primarily to the natural or inherent variability in the corrosion rates and the differences in the dehydration of the gas carried by these pipelines.

Figure 11 summarizes the pipeline failure rate in the Gulf of Mexico OCS region during the period 1967-1997 due to all causes. The dramatic increase in the failure rate in 1992 was due primarily to hurricane Andrew.

Since about 1992, there has been a dramatic increase in the number of pipeline failures due to corrosion. This is believed by some operators to be due primarily to cut-backs in pipeline maintenance budgets and efforts in the 1980's. The increase in failure rates has been noted, and the industry has taken effective measures to reduce the rates since 1994.

The failure rate has ranged from about 5 E-3 per mile-year to 2 E-2 (0.02) per mile-year. Given an 'average' pipeline in the Gulf of Mexico of 10 miles, this failure rate equates to about Pf = 5 E-2 per year to Pf = 2 E-1 per year for a 'typical' pipeline. Current operations indicate a total failure rate of about Pf = 0.01 per mile - year, or Pf = 1 E-1 = 0.1 per pipeline year.

Figure 12 summarizes the historic rate of failure of Gulf of Mexico oil and gas pipelines. Oil pipelines generally have had a higher rate of failure, due chiefly to corrosion caused failures. Gas pipelines had a higher rate of failure in 1992 due to the effects of hurricane Andrew.
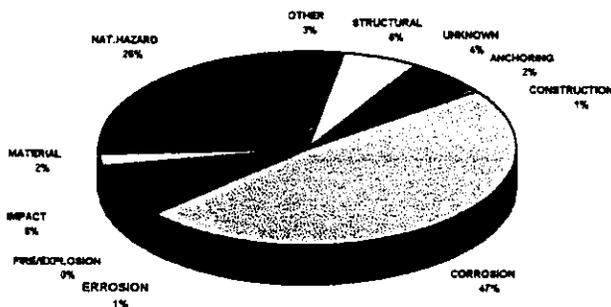

**Figure 6 - Causes of failures of OCS pipelines in the Gulf of Mexico**
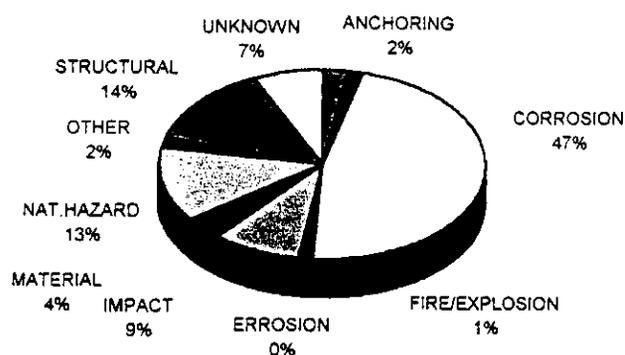
Figure 7 - Causes of failures in gas pipelines
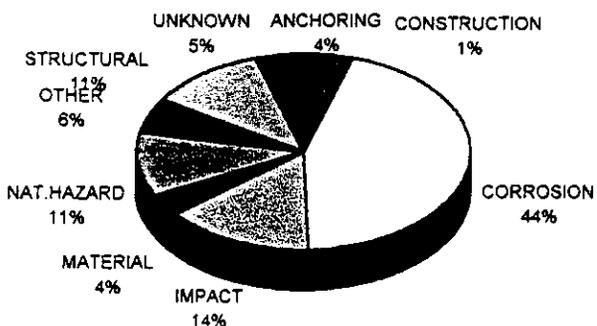
Figure 8 - Causes of failures in oil pipelines
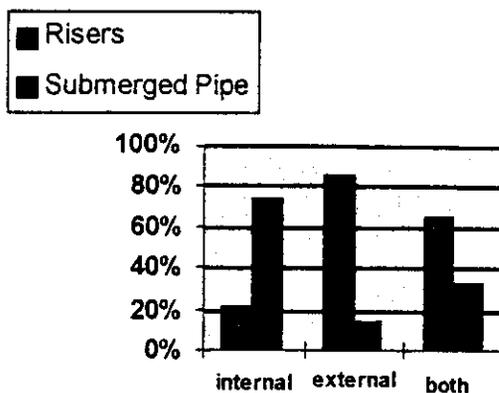
**Figure 9 - Distribution of pipeline and riser failures due to internal and external corrosion**
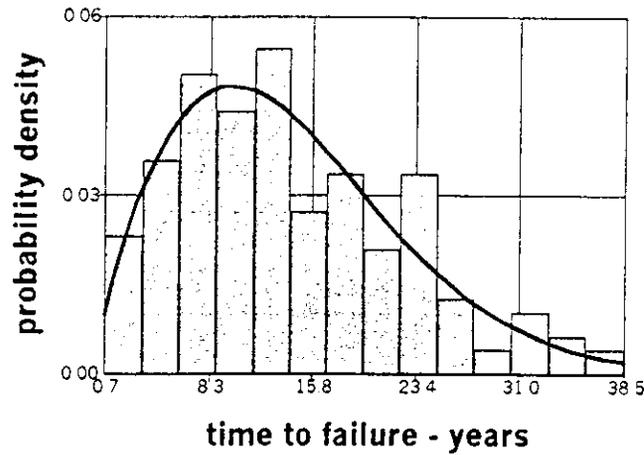
Figure 10 - Distribution of times to failure of gas pipelines due to internal corrosion
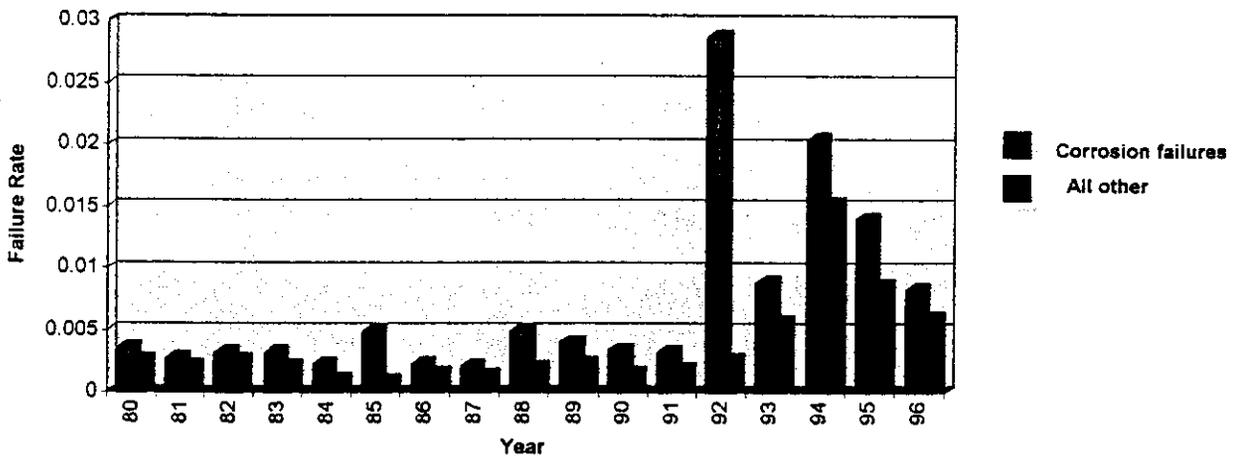
Figure 11 - Historic rate of failure (number of failures per mile - year) of Gulf of Mexico pipelines (OCS area, 1967-1997)
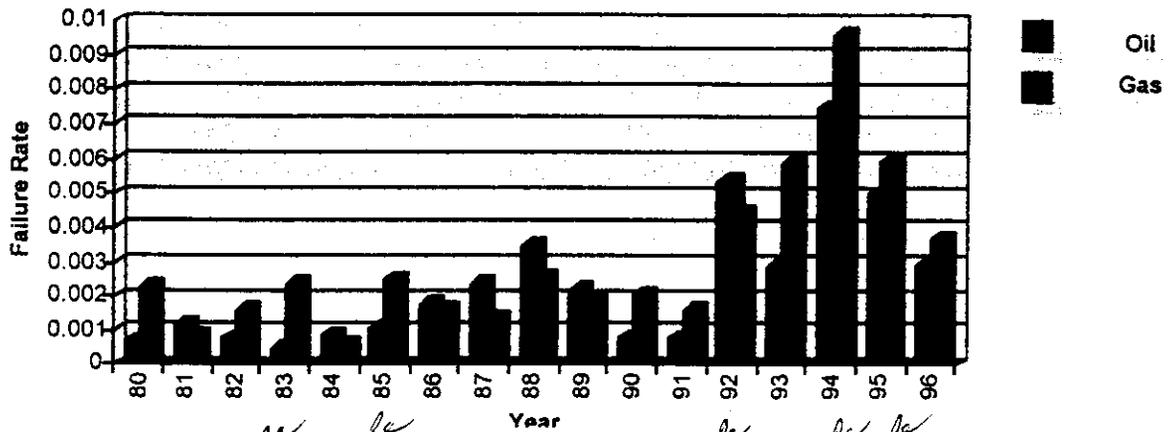

Figure 12 - Historic Rate of Failure of Gulf of Mexico Oil and Gas Pipelines (OCS area, 1967-1997)

Corrosion of steel in pipelines and risers is a function of what is transported in the pipeline or riser, what surrounds the exterior of the pipeline or riser, and how the corrosion is 'managed' (ASME, 1991; Bea, 1992; 1994). A variety of techniques can be used to reduce the rates of corrosion including internal or external coatings, cathodic protection (for continuously submerged segments of pipelines), dehydration of the gas or oil, and the use of inhibitors. Marine growth tends to inhibit or reduce corrosion of risers (NACE, 1992; Kvernvold, et al, 1992).

For this analysis, the loss of pipeline or riser wall thickness due to corrosion (t_c) was formulated as follows:

$$t_c = t_{ci} + t_{ce}$$

where t_{ci} is the loss of wall thickness due to internal corrosion and t_{ce} is the loss of wall thickness due to external corrosion.

The loss of wall thickness due to internal and/or external corrosion ($t_{ci/e}$) was formulated as follows (Elsayed, Bea, 1997):

$$t_{ci/e} = \alpha_{i/e} \, v_{i/e} \, (Ls - Lp_{i/e})$$

where $v_{i/e}$ is the average (mean during service life) corrosion rate, $\alpha_{i/e}$ is the effectiveness of the inhibitor or protection (1.0 is perfect protection, and 10.0 is little effective protection), Ls is the service life of the pipeline or riser (in years), and $Lp_{i/e}$ is the 'life' of the initial protection provided to the pipeline.

This model assumes that there are no inspections and repairs performed during the service life of the pipeline or riser to maintain the strength integrity of the pipeline to carry pressure. Maintenance is required to preserve the protective management measures employed (e.g. renew coatings, cathodic protection, and inhibitors). The corrosion management is 'built-in' to the pipeline or riser at the start of the service period. Inspections and maintenance are performed to disclose unanticipated or unknowable defects and damage (due to accidents).

Stated another way, when an existing pipeline is requalified for service, inspections should be performed to disclose the condition of the pipeline and riser, and then an assessment performed to determined if under the then 'present' condition of the pipeline that it is fit for the proposed service. Alternative management of the pipeline could be to de-rate it (reduce allowable operating pressures), protect it (inhibitors, cathodic protection), repair it (doublers, wraps), or replace it.

Table 1 - Internal (i) and External (e) Corrosion Rates (v) and Variabilities

Descriptor	Corrosion Rate mm/year	Corrosion Rate Variability - %
Very Low	0.001	10
Low	0.01	20
Moderate	0.1	30
High	1.0	40
Very High	10.0	50

For design and requalification , the corrosion rate is based on the owner/operators evaluation of the corrosivity of the fluids and/or gases transported inside the pipeline or riser, and of the corrosivity of the external environment conditional on the application of a certain protection or 'inhibition' program. Table 1 summarizes suggested median corrosion rates, their variabilities (standard deviations of the logarithms of the corrosion rates, approximately the coefficient of variation of the corrosion rates) and the linguistic variables used to describe these corrosion rates (Elsayed, Bea, 1997; NACE, 1992).

Table 3 - Expected Life of the Protective System ($Lp_{i/e}$)or the Service Life of the Pipeline or Riser (Ls)

Descriptor	$Lp_{i/e}$ or Ls (years)
Very Short	1
Short	5
Moderate	10
Long	15
Very Long	≥ 20

For example, a dehydrated sweet gas would generally have a low to very low corrosion rate (0.001 to 0.01 mm/year), particularly if inhibitors were used to protect the steel. A 'normally' dehydrated sweet oil without inhibitors could have a moderate corrosion rate (0.1 mm/year). A pipeline transporting high temperature salt water could have a corrosion rate that would be High to Very High (1.0 to 10.0 mm/year). Sour wet gas without any inhibitors could have similar corrosion rates (in addition to degrading the steel material properties).

A riser in the splash zone in the Gulf of Mexico without coating protection could have a corrosion rate that is High (1 mm/year). This zone would extend from mean low water to about 4 m above mean low water. Below this zone, the corrosion rate would be Moderate (0.1 mm/year), although local riser connections and other elements that could lead to local corrosion or pitting could have a corrosion rate that would be High (1.0 mm/year). An unprotected pipeline could be expected to have an external corrosion rate that would be Moderate (0.1 mm/year), unless there were other factors that could increase this rate (very high water velocities, severe erosion caused by sediment movements).

In this development, the effectiveness of corrosion management is expressed with two parameters, the inhibitor efficiency ($\alpha_{i/e}$) and the life of the protection ($Lp_{i/e}$). If the inhibitor (e.g. coating, dehydration, chemical inhibitor, cathodic protection) were 'perfect', then $Lp_{i/e}$ would equal 1.0. If experience had indicated otherwise, then the inhibitor efficiency could be introduced as summarized in Table 2.

The life of the protection reflects the operator's decision regarding how long the protection that will be provided will be effective at preventing steel corrosion. For example, the life of high quality external coatings in the absence of mechanical damage can be 10 years, where the life of low quality external coatings with mechanical damage can be 1 year or less. Another example would be cathodic protection that could be reasonably provided to protect the pipeline for a period of 10 years, but the expected life of the pipeline was 20 years. Thus, there would be 10 years of life in which the cathodic protection was not provided and the steel would be 'freely' corroding. Table 3

Table 2 - Internal (i) and External (e) Inhibitor Efficiency ($\alpha_{i/e}$)

Descriptor	Inhibitor Efficiency
Very Low	10.0
Low	8.0
Moderate	5.0
High	2.0
Very High	1.0

defines the general categories of the life of protective systems. This same Table can be used to specify the expected service life of the pipeline or riser (Ls).

Given this information, pipeline owner / operators could define the expected life of the pipeline or riser (e.g. Very Long, Ls = 20 years), define the life of the protective management system that would be incorporated as a part of the pipeline or riser (e.g. Moderate, $Lp_{i/e}$ = 10 years), define the effectiveness of the protective management system (e.g. High, $\alpha_{i/e}$ = 2.0), and then based on the transported product and environment of the pipeline or riser, estimate the internal and external corrosion rates (e.g. vi = 0.1 mm/year, ve = 0.1 mm/year). The corrosion thickness allowance would then be determined as:

$$t_{ci/e} = \alpha_{i/e} \, v_{i/e} \, (Ls - Lp_{i/e}) =$$

$$2.0 \cdot 0.2 \, mm/y \, (20 \, y - 10 \, y) = 4 \, mm = 0.16 \, inch$$

This formulation could be expressed in terms of 'effective' corrosion rates ($ve_{i/e}$) and 'exposed life' ($Le_{i/e}$) as follows:

$$t_{ci/e} = ve_{i/e} \, (Le_{i/e})$$

Time Dependent Reliability

Pipeline reliability is a time dependent function that is dependent on the corroded thickness of the pipeline ($t_{ci/e}$). The corroded thickness is dependent on the average rate of corrosion and the time that the pipeline or riser is exposed to corrosion. This time dependency can be clarified with the following (Bea, 1994):

$$\beta = \ln (Kp \, t - Kp \, t_{ci/e})) / \sigma_{lnp/R}$$

where:

$$Kp = (2 \, B \, S / p \, D)$$

If one defines:

$$Kp \, t = FS_{50}$$

where FS_{50} is the median factor of safety in the burst capacity of the pipeline or riser. Then:

$$\beta = \ln (FS_{50} - FS_{50} \, (t_{ci/e} / t)) / \sigma_{lnp/R}$$

As the pipeline corrodes, the reduction in the pipeline wall thickness leads to a reduction in the median factor of safety that in turn leads to a reduction in the Safety Index (or an increase in the probability of failure). In addition, as the pipeline corrodes, there is an increase in the total uncertainty due to the additional uncertainties associated with the corrosion rates and their effects on the burst capacity of a pipeline.

An analytical model for the increase in total uncertainty as a function of the corrosion could be expressed as:

$$\sigma_{lnp/R}|t = \sigma_{lnp/R}|to \ (1 - t_{ci/e} / t)^{-1}$$

where $\sigma_{lnp/R}|t$ is the uncertainty at any given time 't', $\sigma_{lnp/R}|to$ is the uncertainty at time t = 0, $t_{ci/e}$ is the corroded thickness and t is the initial thickness. When $t_{ci/e} / t = 0.5$ the initial uncertainty would be increased by a factor of 2.

Results for $\sigma_{lnp/R}|to = 0.2$ and $= 0.30$ and $FS_{50} = 2.0$ (same as median bias used previously) are summarized in Figure 13.

High quality assurance and control in the pipeline reliability management leads to lower uncertainty and higher reliability (Nordland, et al, 1997). Given corrosion, there is a decrease in the reliability of the pipeline as a function of time reflected in the depth of the corrosion normalized by the wall thickness. If the target reliabilities are defined as those that the pipeline should not be lower than during its life, then either corrosion protection must be provided to preserve the initial thickness of the pipeline or riser, or corrosion allowance must be added to the pipeline or riser initial thickness, or a combination of these two measures. For example, if an annual Safety Index of 2 during the pipeline life were desired, and the initial uncertainty associated with the pipeline demands and capacity were 20%, then the corrosion allowance would need to be 20% of the pipeline thickness. This would result in an initial annual Safety Index of 3.5. Given the projected corrosion rate for the life time of the pipeline or riser, the annual Safety Index would decrease to 2.0 by the end of the projected life.

CORROSION – INSTRUMENTED PIPELINES

Instrumentation or 'smart pigs' can be used to help develop evaluations of corrosion rates and remaining wall thicknesses (Rosen Engineering Group, 1997). These measurements can be used to help make evaluations of corrosion in comparable pipelines that can not be instrumented. Figure 14 shows a probability distribution of corrosion rates determined for the Alyeska pipeline and North Sea oil pipelines. The median values of the corrosion rates are n = 0.06 and n = 0.03 for these two sets of pipelines.

It is important recognize that making evaluations of corrosion rates and wall thicknesses from the recordings have significant uncertainties (Bal, Rosenmoeller, 1997). The measurements can give both 'false positives' and 'false negatives.' The pigs can miss significant defects and indicate the presence of defects that are not present. Figure 15 shows a comparison of the Probability of
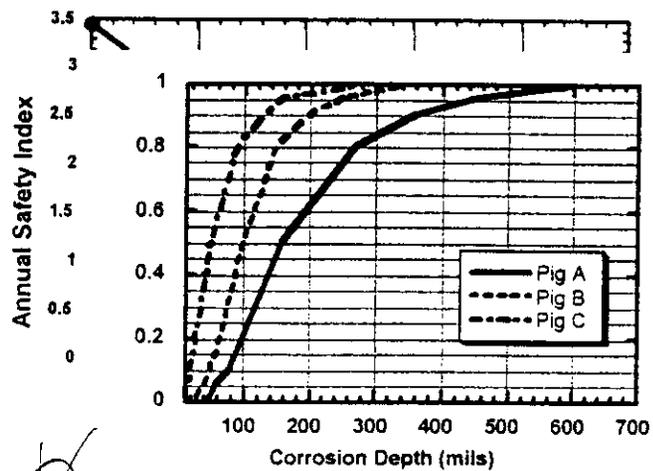
Figure 15 – Probability of Detection Curves for Three Smart Pigs

14

Detection (POD) of corrosion depths (in mils, 50 mils = 1.27 mm) developed by three different 'smart pigs' (Magnetic Flux Leakage, MFL, based instrumentation). This information was based on comparing measured results from sections of the Trans Alaska pipeline that were pigged and then excavated and the true corrosion depths determined (Rust, et al 1996; Vieth, et al 1996). There is a dramatic difference in the performance characteristics of these three smart pigs. If this type of variability is to be avoided or minimized, then specifications and test runs must be developed to verify the ability of the pigs to detect corrosion damage. Specifications for intelligent pig inspections of pipelines need to be developed if consistent and repeatable results are to be realized (Shell International, 1996).
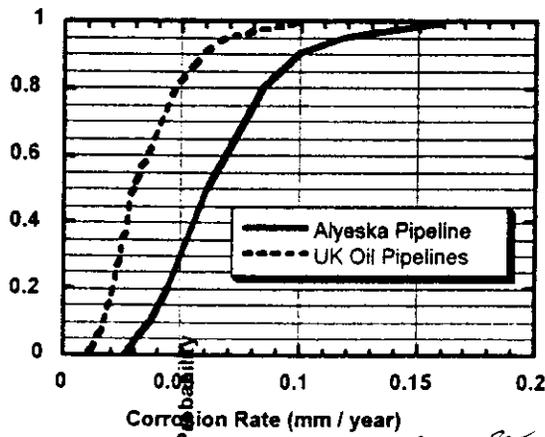
Figure 14 – Corrosion Rates for Two Oil Pipelines

There are significant uncertainties in the depths of corrosion indicated by the pigs due to such factors as variable temperatures and degrees of magnetism, and the speed of movements of the pig (Bal, Rosenmoeller, 1997). Corrosion rates are naturally very variable in both space and time. Thus, if instrumentation is used to determine the wall thicknesses and corrosion rates, the uncertainties in these characteristics needs to be determined and integrated into the evaluations of the fitness for purpose of the


Figure 16 – Bias in measured corrosion depths

pipeline. Figure 16 summarizes data for two of the smart pigs noted in Figure 14. Both pigs tend to under estimate the corrosion depth. The uncertainties associated with the measured depths ranged from 35 % (for 50 mils depths) to 25 % (for 200 mils depths).

For the instrumented pipelines, the expression for the probability of failure can be expressed as:

$$Pf = Pf_D + Pf_{ND}$$

where Pf_D is the probability of failure associated with the detected flaws and Pf_{ND} is the probability of failure associated with the non-detected flaws.

The detected depth of corrosion must be corrected to the median depth of corrosion (Figure 16):

$$t_{C50} = t_{CD} (B_{Dt})$$

The detected depth of corrosion has a standard deviation of the Logarithms of the corrosion depths of:

$$\sigma_{lntc} = 0.25 \text{ to } 0.35$$

Pf_{ND}

The probability of failure associated with the detected depth of corrosion is:

$$Pf_D = 1 - \Phi\{ [\ln (p_{B50} / p_{O50})] / [(\sigma^2_{pB} + \sigma^2_{pO})^{0.5}]\}$$

where Φ is the standard cumulative Normal distribution, p_{B50} is the 50th percentile (median) burst pressure, p_{O50} is the 50th percentile maximum operating pressure, σ_{pB} is the standard deviation of the logarithms of the burst pressure, and σ_{pO} is the standard deviation of the logarithms of the maximum operating pressures.

The pipeline burst pressure is determined from:

$$p_B = 2 S (t - tc) / D$$

The median of the burst pressure is determined from the medians of the variables:

$$p_{B50} = 2 S_{50} (t_{50} - t_{C50}) / D_{50}$$

16

The uncertainty in the burst pressure is determined from the standard deviations of all of the variables:

$$\sigma^2_{lnpB50} = \sigma^2_{lnS} + \sigma^2_{lnt} + \sigma^2_{lntc} + \sigma^2_{lnD}$$

The probability of a corrosion depth, X, exceeding a lower limit of corrosion depth detectability, xo, is:

$$P[\ X \geq xo \mid ND\ ] = P[\ X > xo\ ]\ P[\ ND \mid X \geq xo\ ]\ /\ P[\ ND]$$

P [X ≥ xo | ND] is the probability of no detection given X ≥ xo. P [X > xo] is the probability that the corrosion depth is greater than the lower limit of detectability (Figure 14). P [ND | X ≥ xo] is the probability of non detection given a flaw depth (Figure 15). P [ND] is the probability of non detection across the range of flaw depths (Figure 15) where:

$$P[ND] = 1 - P[D]$$

and:

$$P[ND] = \Sigma\ P[ND \mid X > xo]\ P[X > xo]$$

The probability of failure for non-detected flaws is the convolution of:

$$Pf_{ND} = \Sigma\ [Pf \mid X > xo]\ P[\ X \geq xo \mid ND\ ]$$

Figure 17 shows results from an instrumentation of a 20-inch diameter gas line based on use of Pig C The measured and corrected corrosion expressed as a percentage of the wall thickness is shown. Based these results and foregoing developments, Figure 18 shows the probabilities of burst failure (detected and non-detected) of the pipeline. Two sections of the pipeline would be candidates for replacement.

PRESSURE TEST AND RELIEF EFFECTS

None of these developments have taken account of the effects of pressure testing the in-place pipeline. Based on API guidelines (API, 1993), the pipeline is tested to 1.25 times the maximum design pressure (MDP) for oil pipelines and 1.5 times the MDP for gas pipelines. The maximum
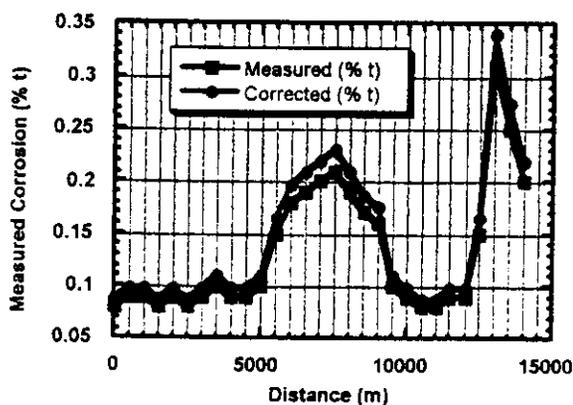
Figure 17 – Pig C measured and corrected corrosion readings
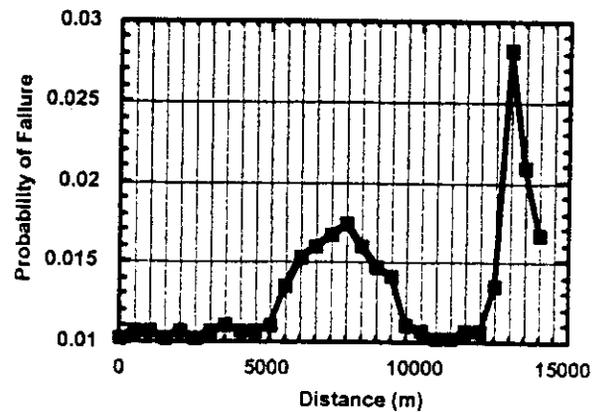
Figure 18 – Probabilities of burst pressure failure

operating pressure (MOP) generally is set at 90 % of the MDP.

The effect of pressure testing is to effectively 'truncate' the probability distribution of the pipeline burst pressure capacity below the test pressure (Figure 19). Pressure testing is a form of 'proof testing' that can result in an effective increase in the reliability of the pipeline.

There can be a similar effect on the operating pressure 'demands' if there are pressure relief or control mechanisms maintained in the pipeline. Such pressure relief or control equipment can act to effectively truncate or limit the probabilities of developing very high unanticipated operating pressures (due to surges, slugging, or blockage of the pipeline).
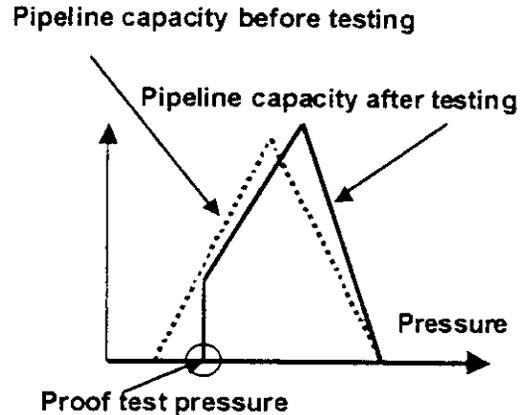
Figure 19 – Effects of proof testing on pipeline capacity distribution

This raises the issues associated with pressure testing and pressure controls on the required factors of safety or load and resistance factors (Hall, 1988; Grigoriu, Hall, 1984; Grigoriu, Lind, 1982). Figure 20 summarizes the results of pipeline proof testing on the pipeline Safety Index as a function of the 'level' of the proof testing pressure factor, K:

$$K = \ln (Xp / p_b) / \sigma_{lnpb}$$

where Xp / pb is the ratio of the test pressure to the median burst pressure capacity of the pipeline (test pressure deterministic, burst pressure capacity Lognormally distributed) and is the standard deviation of the Logarithms of the pipeline burst pressure capacities. These results have been generated for the case where the uncertainty associated with the maximum operating / incidental pressures is equal to the uncertainty of the pipeline burst pressures and for Safety Indices in the range of β = 3 to β = 4.5 (Fujino, Lind, 1977).

For example, if the median burst pressure of the pipeline were 2,000 psi and this had a Coefficient of Variation of 10 % (σ_{lnpb} = 0.10), there was a factor of safety on this burst pressure of 2 (f = 0.5) (maximum operating pressure = 1,000 psi), and the pipeline was tested to a pressure of 1.25 times the maximum operating pressure (Xp = 1,250 psi), the proof testing factor K = -4.7. The results in Figure 20, indicate that this level of proof testing is not effective in changing the pipeline reliability. Even if the pipeline were tested to a pressure that was 1.5 times the operating pressure,
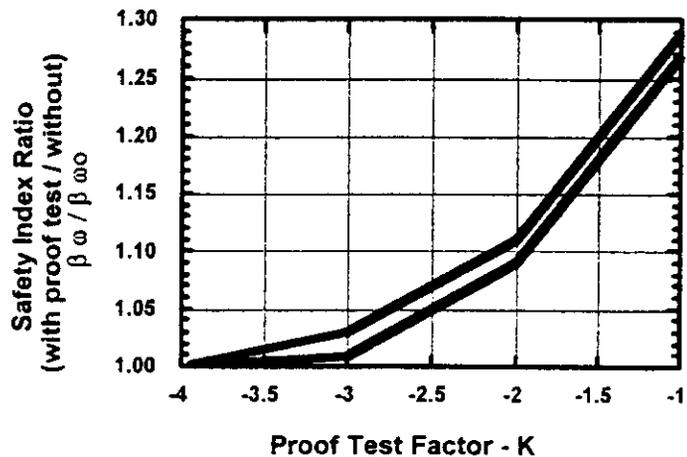
Figure 20 - Effects of proof testing on pipeline reliability

18

the change in the Safety Index would be less than 5 %.

If the test pressure were increased to 75 % of the median burst pressure, the Safety Index would be increased by about 25 %. For a Safety Index of $\beta = 3.0$ (Pf = 1E-3), these results indicate a $\beta = 3.75$ (Pf = 1E-4) after proof testing. Very high levels of proof testing are required before there is any substantial improvement in the pipeline reliability. These results indicate that conventional pressure testing may not be very effective at increasing the burst pressure reliability characteristics. Such testing may be effective at disclosing accidental flaws incorporated into the pipeline due to human and organizational factors (e.g. poor welding).Additional studies are underway to further define the effects of pressure testing and operating pressure controls on the required factors of safety for both new and existing pipelines.

CONCLUSIONS

A general approach for design and requalification of pipeline systems has been proposed that utilizes qualitative, quantitative, and mixed qualitative – quantitative approaches. These approaches are complimentary. The simpler approaches are used to design and requalify the vast majority of pipelines. The more complex approach is reserved for the more complex problems and situations.

The Level 2 approach has been further developed and applied to the evaluation of the burst capacity of corroded pipelines. This approach has addressed pipelines that can not be instrumented and those that can be instrumented. The approach for non-instrumented approach is mixed with qualified – calibrated expert judgement, information from databases on pipeline failures, and data from instrumented pipelines. The approach for instrumented pipelines requires the same information, but in this case, there is more direct information available on the pipeline corrosion characteristics. However, these corrosion characteristics must be carefully evaluated as they are influenced by different qualities of in-pipe instrumentation and the treatment and analysis of the instrumentation results. It is concluded that much more work is warranted to more further develop the Level 2 mixed qualitative - quantitative approaches, particularly for the requalification of existing pipelines.

REFERENCES

American Petroleum Institute (API) (1993). Design, Construction, Operation, and Maintenance of Offshore Hydrocarbon Pipelines (API Recommended Practice 1111, Second Edition, Washington, DC.

American Society of Mechanical Engineers (ASME) (1991). Manual for Determining the Remaining Strength of Corroded Pipelines, Supplement to ANSI / ASME B31 Code for Pressure Piping, New York, NY.

Bai, Y. and Damsleth, P. A. (1997). "Limit-State Design of Pipelines," Proceedings of the Offshore Mechanics and Arctic Engineering Conference, Vol. V., American Society of Mechanical Engineers, NY.

Bai, Y., et al (1994) "Probabilistic Assessment of Dented and Corroded Pipelines", Proceedings International Conference on Offshore and Polar Engineering, Osaka, Japan.

Bai, Y., Xu, T., and Bea, R. G. (1997). "Reliability-Based Design & Requalification Criteria for Longitudinally Corroded Pipelines," Proceedings of the Seventh International Offshore and Polar Engineering Conference, Honolulu, The International Society of Offshore and Polar Engineers, Golden, CO.

Bal, C., and Rosenmoeller, J., (1997). "Can Pipeline Risk Assessment Studies Rely on Rosen Intelligent Pig Surveys?", Proceedings of the International Conference on Pipeline Rehabilitation & Maintenance, Abu Dhabi, UAE.

Bjorney, O.H., Cramer, E.H., and Sigurdson, G. (1997). "Probabilistic Calibrated Design Equation for Burst Strength Assessment of Corroded Pipes," Proceedings of the Seventh International Offshore and Polar Engineering Conference, Honolulu, The International Society of Offshore and Polar Engineers, Golden, CO.

British Standards Institution (1993). Code of Practice for Pipelines - Part 3 Pipelines Subsea: Design, Construction, and Installation, BS 8010, London, England.

British Standards Institution (BSI) (1993). Code of Practice for Pipelines - Part 3 Pipelines Subsea: Design, Construction, and Installation, BS 8010, London,

Collberg, L., Cramer, E. H., and Bjornoy, O. H. (1996). "Re-qualification of Pipeline Systems," Proceedings International Offshore and Polar Engineering Conference, International Society of Offshore and Polar Engineers, Golden, CO.

Elsayed, T., and Bea, R. G. (1997). Pipeline Inspection, Management, and Performance Information System, First Year Report to Joint Industry Project, Marine Technology and Management Group, University of California at Berkeley.

Fujino, Y., and Lind, N. C. (1977). "Proof-Load Factors and Reliability," Journal of Structural Division, Proceedings of the American Society of Civil Engineers, Vol. 103, No. ST4, New York.

Grigoriu, M., and Hall, W. B. (1984). "Probabilistic Models for Proof Load Testing," Journal of the Structural Division, Proceedings of the American Society of Civil Engineers, Vol. 110, No. ST2, New York.

Grigoriu, M., and Lind. N. C. (1982). "Probabilistic Models for Prototype Testing," Journal of the Structural Division, Proceedings of the American Society of Civil Engineers, Vol. 108, No. ST7, New York.

Hall, W. B. (1988). "Reliability of Service-Proven Structures," Journal of Structural Engineering, Vol. 114, No. 3, American Society of Civil Engineers, New York.

International Standards Organization (ISO) (1996). Pipeline Transportation Systems for the Petroleum and Natural Gas Industries, ISO DIS 13623, London, England.

International Standards Organization (ISO) (1996). Pipeline Transportation Systems for the Petroleum and Natural Gas Industries, ISO DIS 13623, London, England.

Jiao, G., Sotberg, T., Bruschi, R., and Igland, R. T. (1997). "The SUPERB Project: Linepipe Statistical Properties and Implications in Design of Offshore Pipelines," Proceedings of the Offshore Mechanics and Arctic Engineering Conference, Vol. V., American Society of Mechanical Engineers, NY.

Kirkwood, M. G., and Karam, M. (1994). "A Scheme for Setting Pipeline Repair, Maintenance and Inspection Priorities," Pipeline Risk Assessment, Rehabilitation and Repair Conference, Pipe Line Industry, Houston, TX.

Kulkarni, R. B., and Conroy, J. E. (1994). "Pipeline Inspection and Maintenance Optimization System (PIMOS), Pipeline Risk Assessment, Rehabilitation and Repair Conference, Pipe Line Industry, Houston, TX.

Kvernvold, O., Johnson, R., and Helgerson, T., (1992) "Assessment of Internal Pipeline Corrosion", Proceedings International Conference on Offshore Mechanics and Arctic Engineering, Vol. 4, American Society of Mechanical Engineers, New York, NY.

Mandke, J. S., Wu, Y. T., and Marlow, R. S. (1995). Evaluation of Hurricane-Induced Damage to Offshore Pipelines, Final Report to Minerals Management Service, Southwest Research Institute, San Antonio, TX.

Muhlbauer, W. K. (1992). Pipeline Risk Management Manual, Second Edition, Gulf Publishing Co, Houston, TX.

National Association of Corrosion Engineers (NACE) (1992). Control of External Corrosion on Underground or Submerged Metallic Piping Systems, NACE RP 0169-92, New York, NY.

Nessim, M. A., and Stephens, M. J. (1995). "Risk-Based Optimization of Pipeline Integrity Maintenance," Proceedings of the Offshore Mechanics and Arctic Engineering Conference, Vol. V, American Society of Mechanical Enigneers, New York, NY.

Nordland, S., Bai, Y. Damslet, P. (1997). "Reliability Approach to Optimize Corrosion Allowance," Proceedings of the Conference on Risk Based Limit State Design and Operation of Pipelines, Aberdeen, Scotland.

Office of Pipeline Safety (1997). Risk Management Program Standard, The Joint Risk Management Program Standard Team, Washington, DC.

Rust, S. W., Vieth, P. H., Johnson, E. R., and Cox, M. L. (1996). "Quantitative Corrosion Risk Assessment Based on Pig Data," Proceedings of the National Association of Corrosion Engineers International Annual Conference and Exposition, Houston, TX.

Shell International Exploration and Production B.V., (1996). Specifications and Requirements for Intelligent Pig Inspection of Pipelines, Version 1, The Hague, The Netherlands, April.

Vieth, P. H., Rust, S. W., Johnson, E. R., and Cox, M. L. (1996). "Corrosion Pig Performance Evaluation," Proceedings of the National Association of Corrosion Engineers International Annual Conference and Exposition, Houston, TX.

Woodson, R. D., and Bea, R. G. (1990). Offshore Pipeline Failures, Report to the National Research Council, National Academy of Engineering, Marine Board, Washington, D.C., Marine Technology and Management Group, Department of Civil and Environmental Engineering, University of California at Berkeley.

Zimmerman, T. J. E., Cosham, A., Hopkins, P., and Sanderson, N. (1998). "Can Limit States Design be Used to Design a Pipeline Above 80% SMYS?", Proceedings of the Offshore Mechanics and Arctic Engineering Conference, Vol. V, American Society of Mechanical Enigneers, New York, NY.

INSPECTION OF PIPELINES BASED C

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Introduction

The worldwide demand for oil and gas has resulted in a substantial increase in the construction of pipelines during last decades, for collecting and transporting the crude oil and natural gas from the production sites to the refining locations, and then to the distribution points for consuming.

Even though carrying large amounts of hydrocarbon products by pipelines is the most safety way of transportation, a pipeline failure has significant implications for operators in terms of lost production; which causes postponed return of investment and economical losses, unfilled sales obligations, etc. When a pipeline failure results in a lost of containment this may lead to human injury and lost of life, pollution to the environment, and sometimes damage to other economical activities.

As a result of a Joint Industry Project which was partially financed by the U.S. Minerals Management Services, a data base has been developed, maintained, and analyzed on the performance characteristics of the Gulf of Mexico pipelines,(Woodson, Elsayed, Bea, 1990) the data base includes pipeline failures from 1967 through 1997. According to published information of this project, the primary cause of pipeline failure is corrosion (either internal or external), 50% of the failures are due to corrosion, 25% are due to Natural Hazards (hurricanes), while the remaining 25% of failures can be attributed to Human and Organizational Factors (HOF). Therefore, great attention has to be paid on corrosion control due to the fact that it is the major hazard in jeopardizing the integrity of offshore pipelines.

Inspection and maintenance activities are regularly carried out in order to secure the pipeline integrity, and to meet regulatory requirements. The cost of inspection and maintenance activities are a significant percentage of the total operation cost, and with the idea of cutting down on this cost, risk analysis tools have been employed for planning of the inspection and maintenance activities. The approaches used in pipeline risk analysis can be classified into two major categories; Qualitative Index Systems and Quantitative Risk Analysis.

The Qualitative Index System has serious drawbacks when used in the inspection and maintenance planning, since this approach is based on indexes which are defined purely on subjective judgements. Index methods assign subjective scores to a pipeline with respect to different factors that influence the probability and consequences of failure then combine the scores, using simple subjective formulas, into an index representing the level of risk.

The risk index is then used as a basis for ranking pipeline segments with respect to each other, without any indication of how the risk associated with these segments compare to tolerable risk level. In the other hand, Quantitative Risk Analysis is based on an objective approach that utilizes data, and structural reliability theory.

An estimation of pipeline reliability as function of time would provide a decision tool to planning, when the following inspection by smart pig has to be carried out or whether a pipeline segment has to be replaced. Therefore data provided by smart pigs have to be utilized in order to estimate the pipeline reliability as a time function.

Objectives of in-service inspections

An offshore pipeline can be considered as system composed of several parts, such as; pipes, external pipeline coating, sacrificial anodes, concrete coating, field joints, and accessories like; valves, tees, flanges, etc. In order to maintain the pipeline integrity along their design life, periodic inspections have to be carried out, mainly divided into two categories as follows:

- Internal inspection
- External inspection

The objective for internal inspection may be to measure the internal corrosion rate or to evaluate the performance of an inhibitor program. For the first case, Weight Loss Coupons, and Electric Resistance are commonly employed, while for the second case some monitoring techniques have been utilized such as; Linear Polarization Resistance, Electrochemical Impedance Spectroscopy, and Electrochemical Noise.

For measuring the internal and external corrosion a smart pigs can be utilized (either magnetic flux leakage or ultrasonic technique).

The external inspection of pipelines is usually done by using ROVs to disclose the condition of the concrete coating, leaks, field joints, depth of burial, and pipe to soil potential are continuously measured along pipelines.

Pipeline inspection by smart pigs

The on-line inspection has evolved from the first generation up to high-resolution smart pigs; last generation smart pigs are now capable of detecting and sizing anomalies than previous pigs could not do.

The high-resolution pigs provide to a pipeline operator a record of metal loss due either to internal or external corrosion. These metal loss varies in magnitude, and location along pipeline length, also there are uncertainties on sizing metal loss with depends on smart pig type.

A general process is presented in Figure 1, in which it is described how the data provided by a smart pig can be used in pipeline reliability.

Figure 1, General process of using smart pig data on reliability estimation

Remaining strength of pipelines based on data collected by smart pigs

In the last two decades metal loss measured by smart pigs are employed in estimating the remaining strength of corroded pipelines, by applying the criteria indicate in ASME B31G Manual for Determining the Remaining Strength of Corroded Pipelines, which is based on a semi-empirical fracture mechanics relationship originally develop by Folias (1967), to simplify the evaluation of a corroded pipeline, the area of metal loss A is usually represented by a parabola as shown in figure 2.

Figure 2, Longitudinal view of a corroded pipeline

So the calculation of A on the basis of two parameters of the metal loss; its length (L) and maximum depth (d), this give A= (2/3)Ld and the non corroded area Ao= Lt, using this and the flow stress equal to 1.1 SMYS, leads to the hoop stress at failure by the following formula:

$$\sigma = 1.1 \, SMYS \left[\frac{1 - (2/3)(d/t)}{1 - (2/3)(d/t)(M^{-1})} \right]$$

Where:

S   Hoop stress at failure
SMYS   Specified Minimum Yield Stress
D   Maximum corroded depth
T   Nominal wall thickness
M   Folias factor

However this criteria has a excessive conservatism mainly due to:

- Expression for flow stress
- Approximation used for Folias factor
- Parabolic representation of metal loss
- Variability of corrosion depth along pipe axis

In recent times the application of finite element methods for estimating the remaining strength of corroded pipelines has received more attention. Several studies have reported that finite element method is suitable to be applied for determining the burst prediction of corroded pipelines, Chouchaoiu and Pick (1994), also this method can be employed to optimize laboratory tests by performing a large number of parametric runs to allow reducing the number of tests.

The use of finite element method has the following advantages:

- Capability to handle complex loading condition; combined loads due to axial force, internal pressure, temperature, and bending
- Complex defect geometry can be modeled
- Accounting for geometric and material non linearity

Probabilistic characterization of corrosion data

The corroded configuration reported by a smart pig is irregular in terms of geometry, and location along pipelines. In addition to this, there are uncertainties on sizing the defects, for instance, some smart pigs are not capable to measuring defects whose axial length are less than twice the wall thickness pipe. The probability of detecting and accurately sizing corrosion defects should be taken into consideration in reliability studies.

In order to treat these measured defects, a spatial random field can be employed. Random fields are spatial generalizations of random processes, and are used to describe spatial variability of parameters such as geometry (Orisamolu, 1996).

Random fields are uniquely define by three attributes:

- Probability distribution
- Statistical parameters
- Correlation over the spatial domain of interests

By using this technique, metal losses can be represented more accurately than by using the parabolic representations of criteria B31G, and also random fields include the spatial and time dependent variability, so a corroded pipeline may be represented as function of time.

Time dependant corrosion damage model

The corrosion of pipelines has to be included in a model that takes into account the corrosion rate as function of time, and considering the following:

- Historical data
- Corrosion rate for a specific type of environment, material and operational conditions

Time dependant reliability models for pipelines

For time-variant reliability problems which are of relevance to the prediction of pipeline reliability with time, level III should be considered.

The time-dependant reliability formulation consists of the description of a time-dependant limit state function, $g(x(t))$, given by:

$$g(x(t)) = R(t) - L(t)$$

Where:

R = Pipeline resistant/strength capacity
L = Load/demand on pipeline

When:

$$g(x(t)) < 0 \text{ denotes failure}$$
$$g(x(t)) > 0 \text{ denotes safety of pipeline}$$

The function $R(t)$ is defined with reference to finite element methods, and taking into account the time dependant corrosion growth.

Conclusion

Additional works have to be done in developing reliability models of pipelines by taking into account the time-dependant function of corrosion growth.

Several research works has been done in Canada, USA and Europe concerning pipeline reliability, and those efforts have to integrate in order to optimize pipeline inspection by smart pigs.

References   next page

Towards optimal inspection strategies for fatigue and corrosion damage, 1997 Transactions of the Society of Naval Architects and Marine Engineers, Jersey City, New Jersey, Dr. K. T. Ma, Dr. I. R. Orisamolu, R. T. Huang, and R. G. Bea.

In service Inspection Programs for Marine Structures, Proceedings 16th International Conference on Offshore Mechanics and Arctic Engineering, American Society of Mechanical Engineers, Yokohama, Japan, 1997, R. G. Bea and T. Xu

Reliability based Design and Requalification Criteria for Longitudinally Corroded Pipelines, Proceedings 7th International Conference on Offshore and Polar Engineering, Honolulu, Hawaii, May 1997, Y. Bai, T. Xu, and R. G. Bea

Probabilistic assessment of dented and corroded pipelines, Proceedings of the Offshore Mechanics and Arctic Engineering Conference, Vol. V, American Society of Mechanical Engineers, NY

Can pipeline Risk Assessment studies rely on Rosen Intelligent Pig Survey? , Proceeding of the International Conference on Pipeline rehabilitation and maintenance, Abu Dhabi, UAE,, Bal C. , and Rosenmoeller J. 1997

Assessment of Internal Pipeline Corrosion, Proceedings of the Offshore Mechanics and Arctic Engineering Conference, Vol. 4, American Society of Mechanical Engineers, NY

Reliability Approach to Optimize Corrosion Allowance, proceedings of the Conference on Risk Based limit state design and Operation of Pipelines, Aberdeen, Scotland, Nordland, S. Bai Y. Damslet P. 1997

A probabilistic approach to Prediction of CO_2 Corrosion, and its application to Life Cycle Cost Analysis of Oil and Gas equipment, Corrosion 95, paper No. 65

Analysis the pressure strength of corroded line pipe, Proceedings of 11th Offshore Mechanics and Arctic Engineering Conference, Vol. 4, American Society of Mechanical Engineers, NY, Bubenik, T A, Olson, R. J., Stephens, D. R. And Fransisni, R. B., 1992

Burst pressure prediction of Line Pipe Containing Single Corrosion pits Using Finite Element Methods, Proceedings of the Offshore Mechanics and Arctic Engineering Conference, Vol. 4, American Society of Mechanical Engineers, NY, Chouchaoui, B. A., Pick, R. J., and Yost, D. B., 1992

Bursts pressure predictions of line pipe containing single corrosion pits using finite element methods, Proceeding of the 14 International Conference on Offshore Mechanics and Arctic Engineering, ASME, Houston, Vol. V. Chouchaoui, B.A. ,Pick, R.J. and Jost, D. B. (1992),

Standard damage-assessment approach is overly conservative, Oil and Gas journal, Vol. 88, No. 16. Couslon, K.E..W and Worthinghaam, R.G. (1990),

Plenary and Special Topic Presentations

Deep Water Corrosion Control Design
J. Britton, Deepwater Corrosion Services, Inc.

The Coming of Age of Titanium for Application to Marine and Offshore Oil & Gas Systems
J.S. Grauman, TIMET - Henderson Technical Laboratory
J. Barber, TIMET - Corporate Development Group

Composite Material Offshore Corrosion Solutions
Jerry G. Williams, CEAC – University of Houston

Economic Considerations in Material Selection for Offshore Oil & Gas Production Applications
D. Pattle, Wyman-Gordon Co.
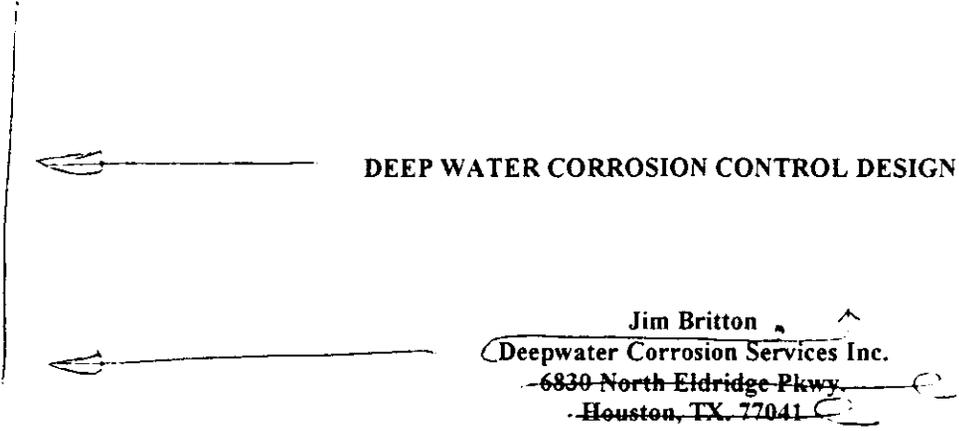
DEEP WATER CORROSION CONTROL DESIGN

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ABSTRACT

Deepwater offshore structures are now quite common, however a deep water development project still requires significant capital investment on the part of the operator. Corrosion failure is not acceptable. This paper presents a common sense approach to cathodic protection design on deep-water projects. Some practical tips for avoiding pitfalls are presented as well as the role of ROV's in maintenance and monitoring of these structures.

Keywords: offshore, cathodic protection, deep water, ROV, cathodic protection monitoring, subsea completions, subsea wellheads.

INTRODUCTION

Development of deep water oil and gas prospects world-wide, has resulted in the emergence of many alternative schemes and structures designed to produce the oil and gas cost effectively. Early developments used large fixed jacket structures such as the Shell Cognac and Bullwinkle platforms, which are located in water depths of 1000 feet and 1350 feet respectively in the Gulf of Mexico. As drilling moved to even greater depths, these fixed structures were no longer cost effective and new structure designs emerged such as Tension Leg Platforms (TLP's), Floating Production Systems (FPS's) and SPAR designs. All of these structures have process facilities located on the surface above subsea wellheads. The completion of remote subsea wells connected by flowlines and control umbilicals to a surface production facility is now common. This is a cost effective method to develop smaller reservoirs. These remote wells are often several miles from the production facility. It is not uncommon for several subsea wells to be connected to a subsea manifold structure, this is in turn connected by pipelines to a production or storage facility on the surface some distance away. These wells, manifolds, flowlines, jumpers and umbilicals are the main focus of this paper.

ENVIRONMENTAL CONSIDERATIONS

Understand Deep Water

There are three major factors impacting cathodic protection (CP) design in deep water. It is important to understand these factors and how they work together to drive CP designs in this environment.

Water Temperature. Temperature decreases with increasing water depth. Temperature has a direct affect on the water resistivity. By affecting the solubility of nutrient salts, lower temperature changes the composition and morphology of calcareous deposits formed at the cathode.

Water Resistivity. The resistivity of seawater increases with increasing water depth. This directly affects the anode to seawater resistance, this increase in resistance decreases current output from anodes of fixed geometry. Water resistivity is therefore a major factor in sizing anodes to meet desirable weight to current ratios.

Calcareous Deposits. Deposits formed on the cathode surface as a result of electrochemical reactions associated with cathodic protection. This phenomenon is the major factor in the success of seawater cathodic protection systems, the calcareous deposit, acting as a barrier coating, has the affect of dramatically reducing current density requirements for cathodic protection. Calcareous deposits form much slower in cold water, and in general are less dense than deposits formed in warmer waters. Less dense deposits require a higher current density to maintain required cathodic polarization.

In summary, design of deep-water cathodic protection systems requires the basic design criteria modification thus;

1. Use higher initial (polarization) and maintenance current density values than would be used in shallow warm water.
2. Use higher seawater resistivity values when computing anode resistance/current output.
3. Use coatings to reduce CP current requirements.

DESIGNING CP SYSTEMS

Basic Considerations

Design Conservatively. If "conservative" is defined as "*being within sensible limits*", then we must design deep water CP systems very conservatively. The cost associated with deep-water oil & gas projects is measured in tens, or even hundreds of millions of dollars. Costs associated with in-situ repairs quickly escalate into millions of dollars, thus corrosion failures are not an option, CP systems for these pieces of equipment have relative costs in the tens of thousands of dollars, CP is cheap use it wisely, get it right first time, every time.

Use Coatings. As previously stated, CP design in cold water presents the following challenges; more cathodic protection current is required per unit area, standard anode geometry will make less current available. When designing, it quickly becomes obvious that covering up some surface area with coatings makes CP designs much more workable. In addition, coatings provide additional benefits associated with in-situ visibility and corrosion protection during onshore fabrication.

Coating Efficiency. What is the appropriate coating breakdown factor to use? This question has been debated among corrosion engineers for decades. Published guidelines vary in their advice on this subject, one prominent code would consider some coatings completely worthless after 20 years [1]. The same guideline later provides a common sense statement " *Operator's experience of a specific paint coating system may justify the use of less conservative coating breakdown factors than specified in this document.*" Clearly conservative common sense must rule, for pipelines, it is common practice to assign a coating breakdown factor of 5% over the design life, for coatings on seawater immersed surfaces near bottom the writer would recommend increasing this numbers to 10-15% initial damage and 20-25% over the design life. This will result in more anodes but remember. Be safe ..... not sorry, you know it makes sense.

Quality Control. It is critical that anodes work as designed. Anodes which fail to activate, or which perform with significantly reduced galvanic efficiency could mean that a premature anode retrofit would be required. An anode retrofit is not out of the question but it will usually be very expensive. Quality anode performance can be guaranteed if the following basic rules are observed:
1. Write a clearly defined specification with special emphasis on electrochemical potential and efficiency testing. Any serious deficiencies in chemical composition will be exposed in these tests. A helpful document has recently been revised by a NACE T7-L technical committee [2].
2. Use an anode alloy with a proven track record. The Al-In-Zn-Si anode alloys are preferable because they have a more predictable behavior in mud environments , have less environmental concerns than Mercury (Hg) or Tin (Sn) activated materials, are more efficient and lighter than zinc anodes and have the highest available open circuit potential of all the viable options.
3. Ensure that the anode specifications require that the testing be performed at the minimum anticipated service temperature.
4. Specify an anode chemistry that will work in cold water, and cold saline mud. A suggested modification of an ambient temperature chemical composition versus one intended for cold water is presented in Table 1. This will result in fewer rejects at the testing phase, and will reduce the risk of anodes not activating when installed.
5. Ex-pect what you In-spect. Use qualified third party inspectors to assure anode quality.

SPECIAL CONSIDERATIONS FOR SUBSEA PRODUCTION EQUIPMENT

General Considerations

The mechanical complexity of a subsea wellhead assembly, or a subsea production manifold causes a number of unusual problems for the cathodic protection designer. The wide array of specialized materials involved in the construction can result in

unexpected compatibility issues for example, it is important to be aware of pitfalls and design the CP systems around them. Some problems unusual to subsea production equipment are addressed in the following sections.

Electrical Continuity. Many of the subsea structures currently being installed have hundreds of individual components and many moving parts. A typical subsea wellhead tree is shown (Figure 1). The anodes for these devices are typically welded to the support frame(s). If all the pieces of the assembly are not electrically tied, with a sufficiently low resistance, to the frame, then the unbonded component is free to corrode at whatever rate applies to that material in seawater. Some causes of discontinuity are:

1. Bolted joining of coated components. This often results in the fastener and one of the two components being out of circuit with the cathodic protection system. This causes special problems if the fastener is made from a material subject to crevice corrosion.
2. Fluorocarbon (Xylan) coated fasteners that are used because of their predictable torque properties, and limited atmospheric corrosion protection, are often left isolated because of the dielectric properties of the coating. Damage to the heads of bolts and nuts from wrenches leave the fasteners to corrode freely.
3. Necessary articulated joints often results in discontinuities across the articulation mechanism.
4. Mechanical connectors and stabbing posts that may appear to guarantee electrical contact can, and have left entire sections of subsea assemblies discontinuous.

Continuity Testing. Most subsea development projects include a phase called System Integration Testing (SIT). All the various components of the system are stacked up or connected on dry land to simulate the completed offshore installation. This is a perfect opportunity to verify electrical continuity throughout the assembly. Continuity is verified from a common test point on the component where the anodes are attached, to all other components that comprise the assembly. A standard multimeter can be used to check the resistance, the author's company recommends that a value of 0.3Ω or less be verified (excluding test lead resistance). The same test points (Figure 2) are used as inspection points for life cycle monitoring of the system. Discontinuities (and there will usually be some), can be fixed onshore quite easily. An example of a typical discontinuity found during an inspection is shown in Figure 3.

Fixing Continuity Problems. Some ways in which continuity problems are addressed are:

1. Tack weld across bolted joints.
2. Use stainless steel wire jumpers between components.
3. Use star (serrated) washers under bolt heads.
4. Remove coatings under bolt heads.
5. Use conductive fastener coatings.
6. Locate anodes on more components.

Material Incompatibilities. The wide array of materials and corrosion resistant alloys used on these projects can cause problems. It is important to review all materials that will be exposed to cathodic protection for their susceptibility to hydrogen damage at the expected potential. Materials that should be closely checked include some alloys of titanium, some stainless steels (400 series for example) and 17-4 PH. Sometimes it is difficult to prevent components from receiving cathodic protection even though the material selection engineer may not have intended it.

Cathodic Shielding. Connectors used to make subsea pipeline connections are extremely intricate mechanical devices with tight, flooded, interior spaces comprising combinations of materials. It is important to remember that concentrated areas of uncoated steel (albeit stainless steel) in metallic compartments may be subject to cathodic shielding, and may not receive enough current to provide adequate cathodic protection. Care should be taken to ensure that these areas are provided with anodes inside and outside the compartment. Other areas potentially subject to shielding include components with mechanically attached dielectric buoyancy modules (syntactic foam), these can behave like ultra-thick disbonded coatings. Control pods often have control tubing manifolds under a protective steel cover. These areas must receive special attention from the cathodic protection designer.

Mud Buried Steel. The mud buried steel, pilings, well casings, mud mats anchors etc., have a surface area which is often an order of magnitude greater than the steel surface in the water zone. In addition to the large area, the surfaces are usually not coated. Even though these areas require significantly lower current densities the large area can amount to a disproportionately high anode weight requirement, and available anode attachment real estate is usually at a premium. Be sure that these areas are accounted for conservatively and consider the following points and design options when accounting for the mud buried area.

1. Use current attenuation models to calculate how far it would be possible for an anode to "throw" current. Don't account for steel areas below this, because the corrosion rate will usually be minimal. The writers company

accounts for only the first 200 feet of pilings and well conductors below the seabed at a maintenance current density of 20 mA/m^2 (2 mA/ft^2).

2. Consider the use of sealed thermal sprayed aluminum coatings (TSA) to reduce current requirement. In this case, the writer suggest using the same current density, still on the first 200 feet, but apply a coating factor of 15% bare.

3. Install attachments on the top of pilings which simplify attachment of cables with an ROV. With this provision in place it is relatively simple to install some seabed anode sleds at a remote location to provide the current to these areas and prevent drain from the close fitted anodes on the subsea equipment. This provision is recommended on all these types of project.

4. Don't forget that pilings have an inside too. The top section of pilings normally extend some distance above the pile guide, they are usually bare steel and thus represent a significant percentage of the seawater immersed bare steel area. Don't forget this! Cathodic protection current will be lost to the inside as well as the outside surfaces of these pilings. Coating of the upper sections of pilings is strongly recommended, sealed TSA coatings will work very well here, they can be applied to both surfaces.

ROV Compatibility. At extreme depths > 1000 feet, all work on the facilities will have to be performed by a Remotely Operated Vehicle (ROV). These machines, while continually improving, are still machines with limited dexterity and a tether / umbilical. To keep the CP design ROV friendly, follow these simple steps:

1. Locate anodes in areas where they will not interfere with ROV operations, and avoid designs that introduce potential snag points for the tether.

2. When locating ROV test points, include a grab rail for the vehicle to hold while monitoring the point. This will reduce wear and tear on the ROV's manipulators and on the monitoring equipment (Figure 2) shows a typical CP test point on a tree, note the grab rail. An ROV stab type current density sensor is shown in Figure 4, note the grab rail.

3. For potential monitoring, provide clearly marked, bare steel test stab locations. The high quality coatings used on many of these facilities do not allow stabbing probes to easily penetrate. Attempting to establish a clean tip contact through a high quality marine epoxy paint could damage the subsea equipment and puts tremendous strain on the ROV hydraulic systems.

4. When specifying CP probes or Current probes select a mount that will easily fit the ROV manipulator and which will require minimum interface to the ROV electronic and fiber optic systems. (Figure 5) pictures a recently developed self contained deep water CP probe designed for operation to 10,000 feet, while requiring no electrical interface to the ROV. A standard tip contact CP probe, which requires surface interfacing, is also shown (Figure 6).

SPECIAL CONSIDERATIONS FOR DEEP WATER PIPELINES

What's Special

Basic design criteria for deep-water pipelines and flowlines are not much different from shallow water systems, but there are more risks associated with deep water. The following suggestions are offered to minimize the risk of problems with these systems. Some of these suggestions would incidentally improve shallow water system reliability also.

Anode Tapers. Most deepwater pipelines are not stabilized with concrete weight coatings, thus the bracelet anodes commonly used are proud of the pipeline, this can result in anode detachment during the lay process due to snagging of the anode on the pipe lay equipment. This problem has been described in a number of papers [3][4]. The use of cast polyurethane tapers to anchor the anode and provide a smooth diameter transition has proven to be a very effective remedy, the location of both anode halves can also reduce the risk of snagging (be sure and figure that all the anodes will arrive on the seabed at the six o' clock position), this is not as favorable as the tapers but may be the only workable solution if anodes have to be attached on the lay barge, these methods are discussed in more detail [5].

Pipe Lay Inspection. The best opportunity to identify and repair problems exists at the installation stage. Technology is available which will verify that anodes are attached to the pipe and that the coating is not badly damaged before the pipe hits the seabed [5]. In addition, the post lay inspection performed by all operators to check the location of the line, is a rarely used opportunity to verify that all's well with the pipeline corrosion control systems. Specify that a CP probe be attached to the ROV during the post lay (as built) inspection run.

MONITORING WITH ROV's

Introduction

Without the ROV there would be no oil and gas development in water depths greater than 1500 feet. These underwater robots are complex machines without brains, we have to make it simple for them to do the work of corrosion technicians. The role of ROV's in corrosion monitoring is further discussed [6]. With subsea developments we do not have the luxury of running cables to the surface, we therefore must use the ROV. ROV operable equipment is now available to perform the following tasks:

Potential Surveys. A wide range of equipment is available for point and continuous potential surveys on the subsea equipment and the associated pipelines.

Current Density and Anode Current Measurement. Historically this has been achieved using the electric field gradient method [7]. A newly developed fixed monitoring improvement allows a current density monitor or monitored anode to be deployed for measurement with an ROV (Figure 4), by stabbing a self contained readout into the fixed contacts the voltage drop shunt can be accurately recorded. This system will provide important in-situ, repeatable, steady state polarization data to be used in future CP design improvement.

CONCLUSIONS

Be safe .... not sorry! Pay close attention to the structure, it's continuity, what it's made of, it's geometry and how it will be protected over it's life cycle. Be conservative in coating and CP designs, but make retrofit provisions by providing simple ROV attachment points. Ensure that only quality materials are used in the corrosion control system and last but not least .... Hire a corrosion engineer to review all the design specifications, coatings vs. materials vs. CP.

REFERENCES

[1]   Det Norske Veritas (DnV) – Recommended Practice RP B401 – "Cathodic Protection Design" - 1993
[2]   NACE International – TM0190-98 – "Impressed Current Test Method for Laboratory Testing of Aluminum Anodes"
[3]   CORROSION '97 – Paper 470 – R.H. Winters, A. Holk – "Cathodic Protection Retrofit of an Offshore Pipeline"
[4]   CORROSION '93 - Paper 527 – I.J. Rippon et al. – "Shorting Pipeline and Jacket Cathodic Protection Systems"
[5]   Offshore Magazine April 1996 – J. Britton – "Protecting Pipeline Corrosion Control Systems During Pipe Lay"
[6]   Underwater Magazine – Fall 98 P. 47 – J. Britton – "An ROV interface for Corrosion Monitoring Equipment"
[7]   CORROSION '92 – Paper 422 – J. Britton "Continuous Surveys of Cathodic Protection System Performance on Buried Pipelines in the Gulf of Mexico"

Element	Typical	Cold Water
Iron (Fe)	0.10% max	0.007% max
Zinc (Zn)	2.8 – 7.0%	4.75 – 5.75%
Copper (Cu)	0.006% max	0.005% max
Silicon (Si)	0.20% max	0.10% max
Indium (In)	0.01 – 0.03%	0.015 – 0.025%
Cadmium (Cd)	Not Specified	0.002% max
Others (each)	0.02% max	0.02% max
Aluminum	Remainder	Remainder

Table 1 – Anode Chemistry for Cold Water

Figure 1. Typical Subsea Wellhead Assembly

Figure 2. C.P. Test Pont on Upper Left Corner of Panel
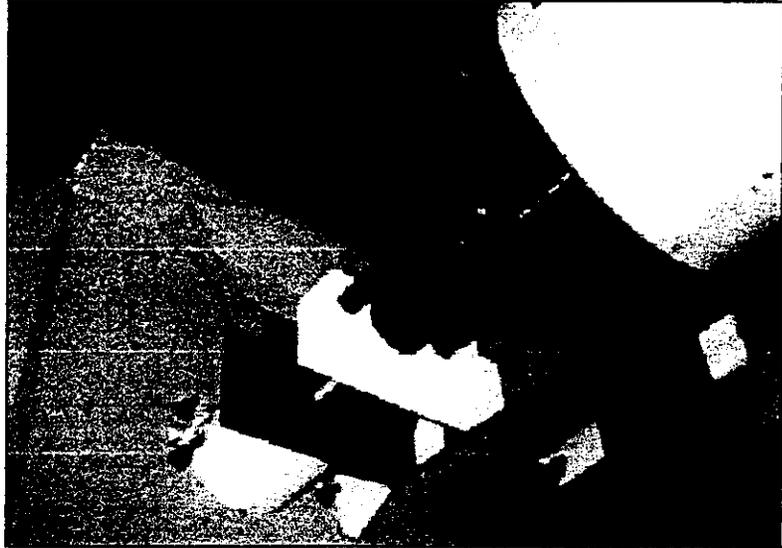
Figure 3. Typical Electrical Discontinuity Across Linkage Mechanism
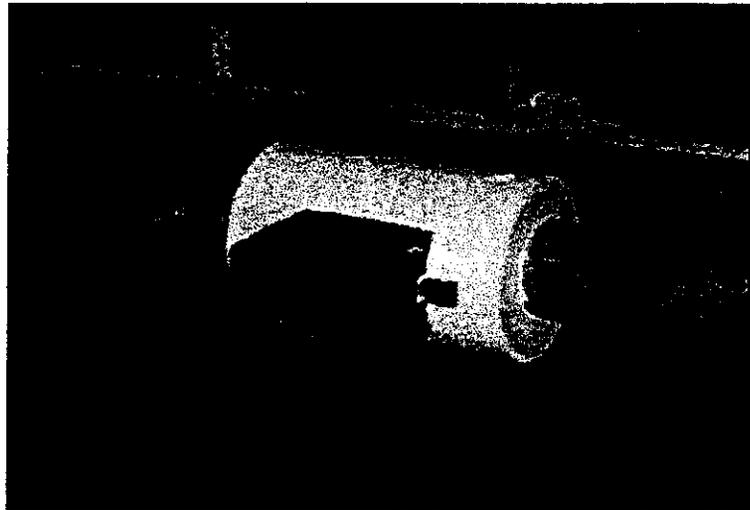
Figure 4. ROV Stab on a Current Density Sensor – Grab Rail on Left
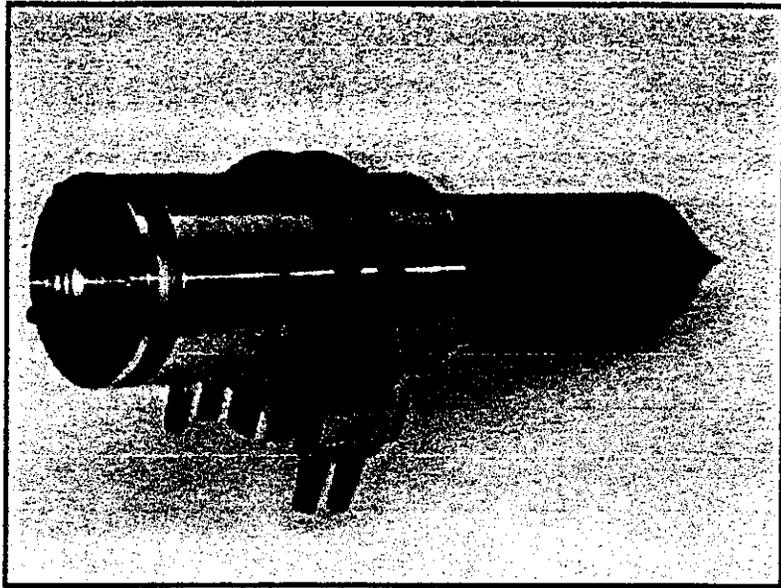
Figure 5. 10,000 Feet Rated Self Contained CP Probe
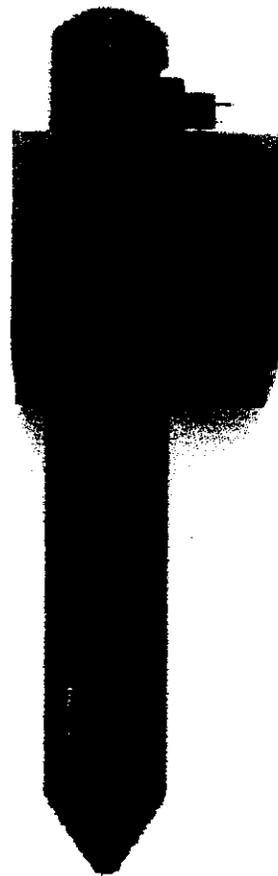
Figure 6. Standard Dual Element ROV CP Probe

The Coming of Age of Titanium for Application to Marine and Offshore Oil & Gas Systems

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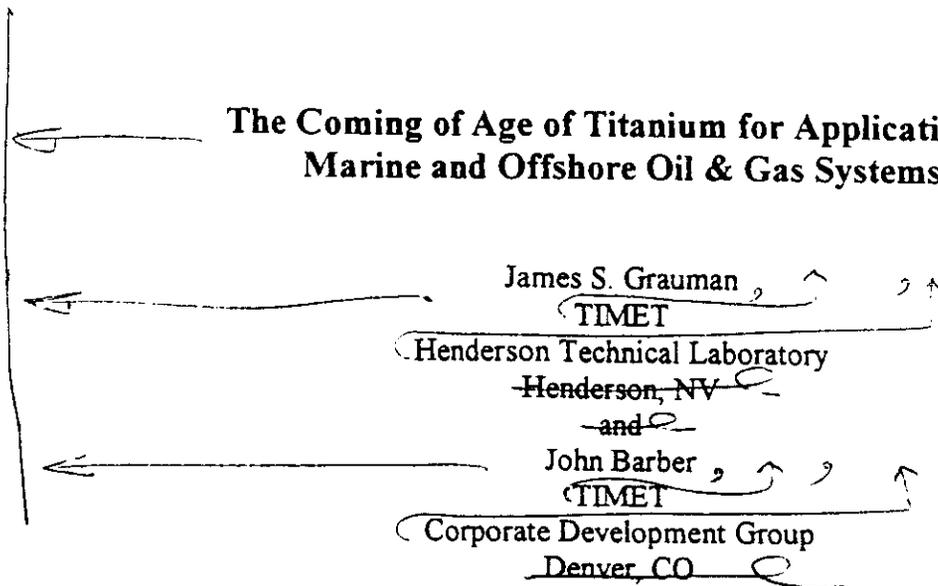
ABSTRACT

The breadth of titanium applications into marine and offshore oil & gas systems is rapidly gaining notice. Marine applications like naval surface ship fire water piping and offshore platform (topside and subsea) applications continue to grow as service experience is favorable. Titanium is now on the verge of being selected for production risers, by far the most ambitious use yet of the attributes of titanium. This paper focuses on the general characteristics of titanium and titanium alloys that have spurred interest in developing applications in sea water and oil & gas produced fluids the last 15-20 years. In addition, some of the current and near term uses are outlined with an eye toward understanding why titanium was selected.

INTRODUCTION

Titanium and titanium alloys exhibit unparalleled corrosion resistance to aqueous chloride media and in particular sea water. This has been the overwhelming reason behind the majority of titanium applications in the industrial sector, such as in coastal refineries and chemical plants, chlorine and chlorine dioxide production, pulp and paper, desalination, and power generation. Over 400 million feet of titanium power plant condenser tubing is in service today, some of it for over 30 years, without a single incidence of corrosion. Over 30 years of experience in refinery environments has demonstrated titanium's excellent resistance to hydrocarbons and other crude oil constituents as well.[1] Titanium has, for more than 20 years, been considered as a viable material for use in offshore oil & gas production systems.[2] In fact, titanium heat exchangers have been in operation on offshore platforms for more than 15 years.

This has involved the use of commercially pure and ASTM grade 12 titanium in shell/tube and PHE (Plate/frame Heat Exchanger) sea water coolers. Further consideration for using titanium has been in part driven by the increasing water depth of platforms where topside weight becomes a critical commodity. Total North Sea titanium usage now well exceeds 2000 MT.[3] In all likelihood, that figure could easily double within the next five years.

As is usually the case for all heavily engineered designs, needs drive new innovations. This has certainly been the case for titanium use offshore as increased demands have led to stable pricing and availability, an increased fabrication base working with titanium and ever decreasing costs of installation. Increasing usage within the CPI and the navy has been due to more awareness and 'comfort level' with the metal, as well as increasingly tight environmental regulations and maintenance costs associated with corrosion.

Commensurate with the increased level of interest in titanium, much work has been done the last five years with respect to corrosion, SCC, galvanic issues, seamless and welded pipe production, cold bending, and welding of titanium and titanium alloys. This work has been instrumental in keeping titanium at the forefront of material selection for new marine, naval, and offshore field developments. In addition, titanium is now frequently being considered the most economic material (on a first cost basis) in many of these applications. Favorable performance in new applications quickly lead to further use of the metal. The near term potential for huge quantities of titanium alloy tubulars being put into service is coming more clearly into focus. This overview paper attempts to put into perspective the current understanding of titanium and titanium alloy characteristics, economics, and applications and looks ahead to titanium's continued growth into ever new areas of marine and offshore oil & gas production.

GENERAL CHARACTERISTICS

Table I lists the grades of titanium suitable for service in general marine and offshore environments. Though not an exhaustive list of titanium alloys, this group does offer proven SCC resistance in chloride environments. All of these grades possess a minimum suite of corrosion properties similar to or better than commercially pure titanium. In addition, each grade has some unique characteristic that could be utilized in offshore oil and gas production systems.

Commercially pure ASTM grade 2 titanium has been and will continue to be the mainstay of the titanium family. Its immunity to corrosion in most sea water applications along with its other attributes of formability, shock resistance, low density, and weldability ensure that it will continue to be the most widely utilized grade. Grade 2 titanium is also the most readily available grade, offering substantial inventories of all mill products, as well as ex-stock piping components from 25-400 mm diameters, as seen in Figure 1. In addition, fabrication of grade 2 titanium is no longer the 'black art' it was once considered to be. As more fabricators become experienced with titanium, components are being scaled up in size to accommodate the increasing demands for the material. Vessels of 4-5 m diameter by 35 m length have been fabricated, as well as pipe components up to 1500 mm in diameter. An example of these components is shown in Figure 2.

Table I. Titanium for Marine and Offshore Oil & Gas Production

Nominal Composition	ASTM Grade	UNS Desig.	Alloy Type	NACE Approved	Strength	Crevice Temp. Threshold	Attributes
Unalloyed Titanium (CP)	1 2	R50250 R50400	Alpha	No Yes	Low	80°C	Most formable grade. Most widely used grade.
Ti-0.05Pd	16	R52402	Alpha	No	Low	>250°C	Added corrosion resistance over grade 2
Ti-0.3Mo-0.8Ni	12	R53400	Lean Alpha/Beta	Yes	Medium	>200°C	Added corrosion resistance & strength vs grade 2
Ti-3Al-2.5V	9	R56320	Lean Alpha/Beta	No	Medium	80°C	Intermediate properties between grades 2 and 23
Ti-3Al-2.5V-0.1Ru	28	R56323	Lean Alpha/Beta	Yes	Medium	>250°C	For added corrosion resistance
Ti-5Al-1Sn-1Zr-1V-0.8Mo-0.1Si	32	R55111	Lean Alpha/Beta	No	High	80°C	High toughness/weldable alloy for plate/fasteners
Ti-6Al-4V-0.1O (ELI)	23	R56407	Alpha/Beta	No	High	80°C	Low oxygen grade 5-no SCC but lower strength
Ti-6Al-4V-0.1O-0.1Ru	29	R56404	Alpha/Beta	Yes	High	>250°C	Added corrosion resistance over grade 23
Ti-6Al-2Sn-4Zr-6Mo	---	R56260	Alpha/Beta	Yes	Very High	>200°C	High strength and good corrosion resistance
Ti-15Mo-2.7Nb-3Al-.2Si	21	R58210	Beta	No	Very High	>250°C	High strength and good corrosion resistance
Ti-3Al-8V-6Cr-4Zr-4Mo	19	R58640	Beta	Yes	Very High	>200°C	High strength and good corrosion resistance

Of the high strength alloys, R56260 and grade 19 have extensive service history in the oil and gas sector, mostly as downhole tubular, logging and wireline equipment. Grade 23 has service exposure as riser components for offshore oil and gas use. These alloys have all given excellent service in these environments. Grades 19 and 29 also have several years experience as production casing in hypersaline geothermal wells, again with excellent performance.
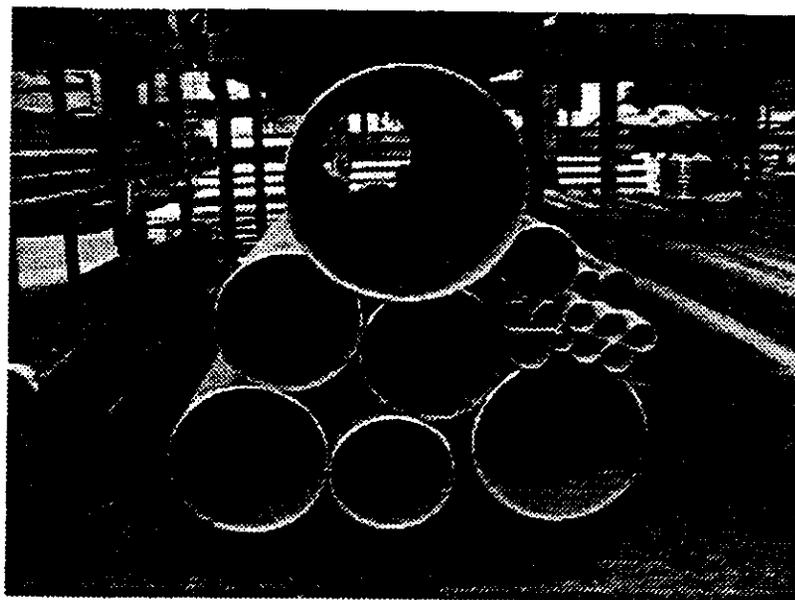
Figure 1. Unalloyed titanium pipe in various inventory sizes.
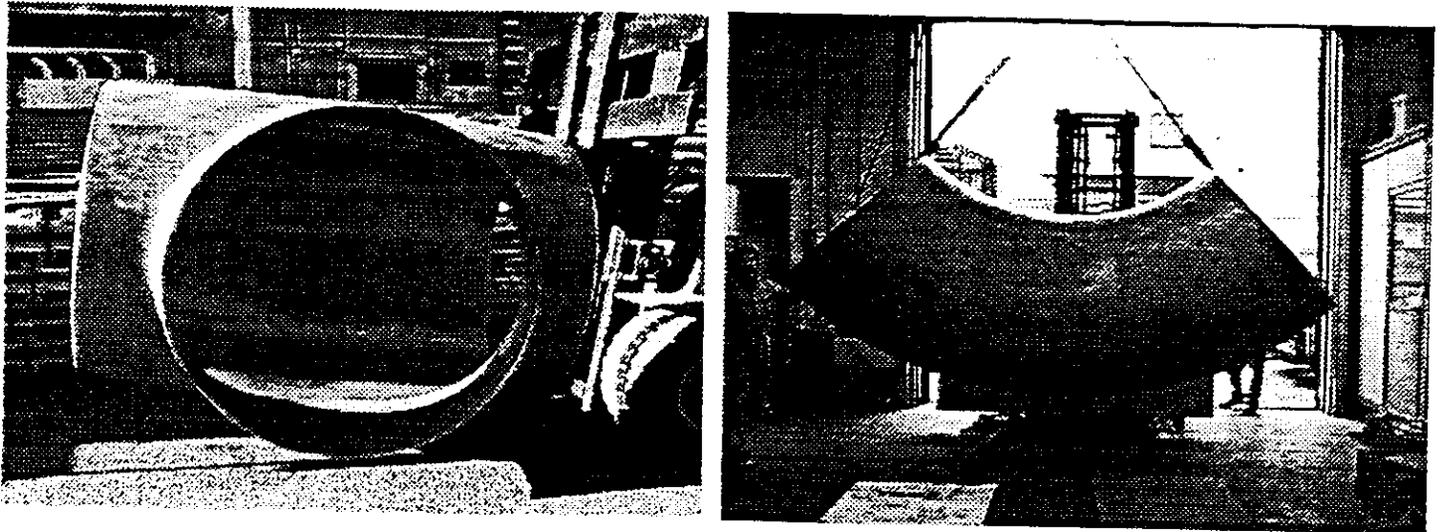
Figure 2. Large diameter grade 2 titanium pipe tee and elbow.

The other grades have specific characteristics that could be utilized from either an enhanced corrosion or mechanical property viewpoint. Figure 3, which illustrates the strengths of these grades, as well as Table I, briefly describe each grade's main attributes. The individual characteristics that apply to offshore and marine environments in general, have been cataloged in another publication.[4]
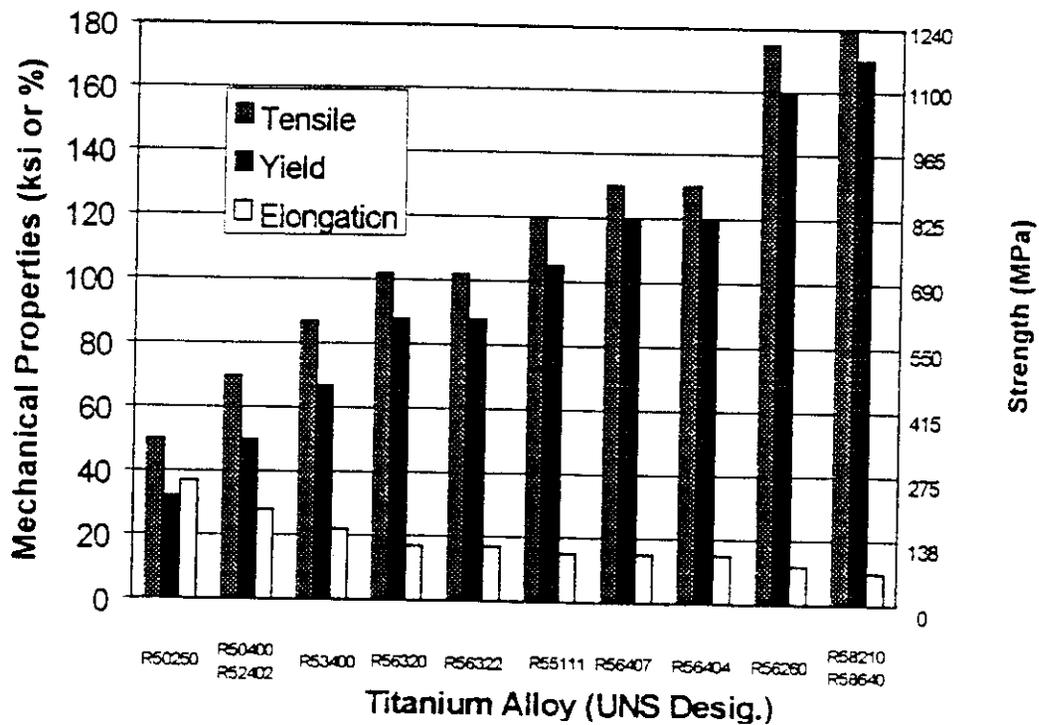
Figure 3. Typical mechanical properties of titanium and titanium alloys for general marine and offshore oil and gas service.

ENVIRONMENTAL BEHAVIOR

Corrosion resistance of titanium has been the driving force for its use in the marine environment industry sector. Titanium is classified as a reactive metal, relying on the formation of a protective oxide film for corrosion resistance. The film is titanium dioxide, a hard, tenacious oxide which forms instantaneously upon contact with air or moisture, and is stable over an extremely wide range of pH and potentials. By studying the nature and stability of the oxide film, one understands much of the corrosion behavior of titanium metal. The scope of this paper does not allow for an in-depth perspective on titanium's sea water corrosion behavior, but rather a general overview. Excellent sources exist for a more detailed examination of the corrosion behavior of titanium and its alloys.[5,6]

General Corrosion, SCC, and Erosion

Titanium is immune to general corrosion attack in all natural, cooling tower, and high purity waters (including sea water and brackish water) to temperatures in excess of 300°C. Contaminants, such as metal ions, sulfides, sulfates, carbonates, and chlorides do not affect the passivity of titanium in marine environments. Exposure of titanium for years at various ocean depths has shown it to be immune to corrosion in ambient temperature sea water (rates < 0.01 mpy). Utilities have, over the last 30 years, installed over 400 million feet of titanium tubing in sea water cooled condensers without a single incidence of corrosion. There has also never been a reported incidence of microbiologically influenced corrosion (MIC) attack on titanium. Titanium is widely regarded as the only common structural engineering metal to be immune to MIC attack. Continued high temperature (>90°C) exposure of titanium to water or steam may produce a slight discoloration of the surface. This is caused by surface oxide growth, and does not damage the integrity of the metal. On the contrary, enhanced oxide films on titanium have been shown to be beneficial in lowering corrosion rates.

Chloride-based stress corrosion cracking has been investigated at length in both sea water and produced fluids. Alloy systems have been set forth based on the SCC testing that fully ensure compatibility. This includes commercially pure grades of titanium for use in navy shipboard and topside on offshore platforms as well as titanium alloys for use in subsea and high stress applications. Extensive service history is now available on grades 1, 2, 7, 12, 19, 23, and 29, and alloy Ti-6Al-2Sn-4Zr-6Mo. There has not been any sea water SCC occurrences reported with the use of these titanium grades despite over 30 years exposure history for some of them in marine environments. All titanium grades are, however, susceptible to SCC in a very few, specialized environments.[7] The one media that is of concern for oil & gas production is methanol. SCC failures of titanium have been reported in absolute (dry) methanol, particularly in the presence of chlorides and/or acid. Moisture in the methanol acts to inhibit the titanium against cracking. Historically, 2% moisture has been given as a safe water content for unalloyed titanium being used for industrial applications involving methanol. Titanium alloys, however, can require higher moisture contents to achieve full passivation. Recent work has shown that regardless of alloy or condition, 10% moisture is sufficient to inhibit any methanol SCC.[8] This level may be reduced, even halved, for alloys like Ti-6Al-4V, under certain conditions of service offshore.

Titanium, in general, demonstrates excellent erosion resistance in many different media, including sea water and produced fluids. The hard and tenacious oxide film proves to be a formidable barrier to erosion, despite being only angstrom's thick.. In sea water, where titanium's oxide film is extremely stable, over a velocity range of 0-35 m/s, titanium is fully resistant to attack. This equals or surpasses the erosion resistance of stainless steel and nickel alloys, which can suffer a combination of general mass loss, pitting, and crevice corrosion depending on velocity.[4,9] In tests involving abrasive aqueous slurries, titanium again proved to be a superior material when compared to high strength steels, stainless steels, and high nickel alloys.[10] Titanium has also been studied in a series of actual and simulated West Texas crude oils.[11] In some of the tests, 3% NaCl and sand was added to the crude to increase the erosive character of the fluid. Unalloyed titanium proved superior to several high strength steels at flow velocities up to 12 m/s and with impingement studies employing both natural gas and air. It was found to perform equally well with stainless and nickel alloys, all of which were free from any attack. The study included field tests as well and again the titanium remained free of any attack during the trial when placed within the producing fluid stream. However, it was found that in cases of erosive wear conditions, such as ball valves, the unalloyed titanium could be subject to erosive wear, sometimes at accelerated rates over high strength steels. For specific applications involving wear, as in valve ball and seat components, hard facing of titanium alloys has been shown to be very effective in increasing the durability of the components.[3]

Localized Corrosion

Titanium is fully resistant to crevice corrosion in sea water and other chloride containing media up to temperatures of about 80°C.[6] Operating temperatures in excess of this may require use of a more resistant grade of titanium, as outlined in Table I, which can provide resistance to temperatures in excess of 250°C. Proper grade selection eliminates concern for localized corrosion of the titanium. However, for existing borderline applications or if material availability becomes an issue, well proven mitigation techniques are available to minimize the overall possibility of localized attack.[12]

Galvanic Corrosion/Hydrogen Absorption

Titanium and its alloys form extremely stable oxide films when exposed to the environments most commonly dealt with in marine and offshore systems. This includes sea water as well as commonly encountered chemical process streams and produced fluids. This passivity yields a noble metal potential in these environments and thus, in most dissimilar metal couples, titanium will act as the cathode. The direct result of this is that titanium is not subject to galvanic corrosion, which is desirable considering the fact that titanium is often used in critical operating equipment. As the cathode, however, titanium can influence the corrosion of the coupled material, with increases in the rate depending on surface area ratios and process media. Interestingly though, the galvanic effects of titanium are usually much less than for other noble metals due to the ease of polarization for titanium. This effect minimizes the overall corrosion acceleration of the anodic metal and in some cases produces negligible increases.[13]

The conservative approach to galvanic corrosion is to assume that some accelerating effect will be present that needs to be eliminated or at least minimized. Several effective

techniques can be utilized to this end.[14] Perhaps the most practical remedial technique is coating of the cathode (titanium). This technique has already been successfully used on titanium offshore components with rubber based, polyurethane, and epoxy resin coatings.[15] Another technique is to use a 'waster' or heavier gage, section of the anodic metal that can be easily replaced on scheduled maintenance outages. Electrical insulation is also a possibility through means of flange type or monobloc isolating joints that interrupt the metal to metal connectivity.

Many different studies have been performed in an effort to give practical guidelines for avoiding hydrogen related problems with titanium when under cathodic potentials.[16,17] If metal wall temperature is low (<70°C), hydrogen embrittlement has been shown to be difficult to achieve due to the negligible diffusion that can occur at these low temperatures. It is important to keep in mind the distinction between absorption and embrittlement. Absorption can occur independently from embrittlement. The reverse is not true. There are indeed many cases of hydrogen absorption in titanium that have never led to embrittlement. Besides the grade, other influencing factors for hydrogen absorption include pH, temperature, degree of aeration, surface condition, chemistry, and metallurgical condition. The critical factors that determine if embrittlement can occur are temperature, stress, and metallurgy (alloying, heat treat, etc.).

Based on all the test studies, a very conservative and practical cathodic potential limit to focus in on appears to be -800 to -900 mV (SCE), as opposed to the current sacrificial anodes which generate -1050 mV.[18] This will allow for adequate protection of the steel (or other anodic metal) while eliminating any concern for hydrogen damage to the titanium.

ECONOMICS

Titanium has always been viewed as a technically correct material for sea water service based on its excellent corrosion behavior. However, many times it has not been selected because of the higher price per pound when compared against carbon steel, copper/nickel, and austenitic stainless steels. Even when life cycle costing demonstrates considerable savings with titanium, the initial capital expenditure has, in the past, remained a formidable hurdle.
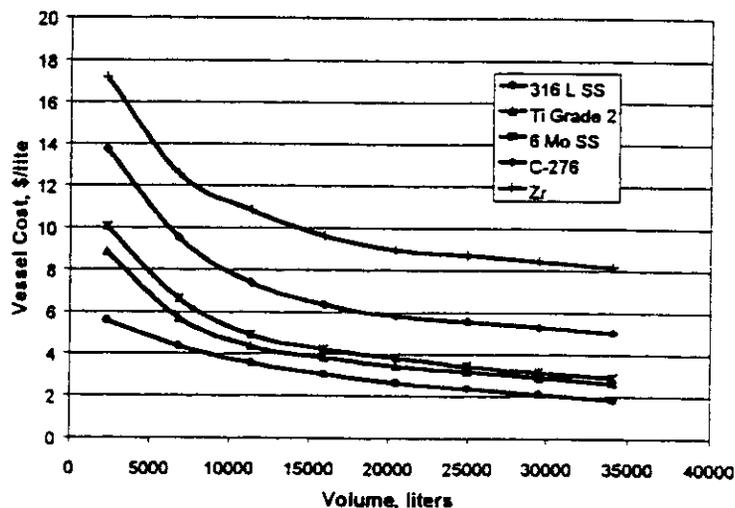

Figure 4. Total cost (material and fabrication) comparison between common engineering metals for typical chemical process reactor vessels.[19]

Despite this seeming obstacle, the titanium industry pressed on and in the last few years has seen a growing trend of titanium usage because it has been competitive on a <u>first cost</u> basis. This has occurred due to many factors, including: titanium price stability, product development, increased fabricator base, more stringent environmental regs, and innovative design engineering. A recent article in Chemical Engineering outlined detailed cost analysis for heat exchangers and vessels. As seen in Figure 4, titanium is nowadays very cost competitive with other common engineering materials.[19] An identical trend is seen with costs for shell/tube heat exchangers.

TITANIUM APPLICATIONS

Heat exchangers and chlorinators were the first offshore uses of titanium some 20 years back. As rigs became larger and more weight sensitive, use of titanium increased at a rapid pace. Today's North Sea platforms will consume somewhere between 300-500 MT on topside applications alone. Titanium riser systems would utilize an additional 500+ MT/platform. Table II outlines some of the varied uses titanium has seen on offshore oil & gas platforms to date. Offshore component replacement costs are estimated at 27X similar onshore costs. Also, approx. $150K can be saved in costs for every ton of weight removed topside.[18] It becomes clear to see why use of titanium is now viewed as critical for economic reasons.

Table II. Titanium Applications Offshore

Platform	Service Use	Ti Grade (Alloy)	Company
Green Canyon	Taper Stress Joints	23 (Ti-6-4 ELI)	Placid Oil
Oryx	"	"	Oryx Energy
Sleipner	Sea Water Lift Pipe	CP Ti	Statoil
Sleipner West	Fire Water System	CP Ti	"
"	Penetration Sleeves	CP Ti	"
Veslefrikk	Sea Water Lift Pipe	CP Ti	"
Heidrun	Drilling Riser	23 (Ti-6-4 ELI)	Conoco
"	Booster Lines	9 (Ti-3-2.5)	"
"	Anchor System Piping	CP Ti	"
Statfjord	Penetration Sleeves	CP Ti	Mobil
Statfjord A/B	Ballast Water System	CP Ti	"
Brage	Fire Water System	CP Ti	Norsk Hydro
Troll Olje	"	CP Ti	"
Oseberg	Penetration Sleeves	CP Ti	"
Hibernia	Ballast Water System	CP Ti	Hibernia
Froy TCP	Fire Water System	CP Ti	Elf Petroleum
Frigg	Fresh Water Piping	CP Ti	"

Risers

The first taper stress joint was installed in 1983 in the Gulf of Mexico. Since then an additional 15 joints have been ordered/supplied. The first titanium drilling riser was put in operation in 1993. All of these components have performed without any mechanical or corrosion failures. 1999 will see the use of the first titanium export riser and the industry could well see the first titanium production riser system installed the following year.[3]

Water Piping Systems

Titanium has become the preferred material for construction of fire water systems since insurance underwriters put increasing pressure to bear on oil companies to increase the fire safety protection on the platforms. Uninsulated titanium piping has successfully passed the NPD H-class hydrocarbon fire test.[20] The high damage tolerance exhibited by titanium provides maximum survivability in the event of a disaster. Fire system manufacturers supplying to offshore platforms now offer complete titanium fire systems including sprinklers, detectors, valves, nozzles and piping. Design engineering in terms of pipe wall and cold forming allow economical system installations. Titanium systems are now in operation on several platforms.

Titanium is becoming accepted as the most economical material for all piping systems (fresh and saline) due to the reduced manpower and equipment costs needed to install these systems. A study conducted by Elf Petroleum concluded that titanium was the most economical (on a first cost basis) pipe material up to 8in. diameter, even when compared to carbon steel. Cold bending of the pipe to minimize connections, along with reduced costs (due to weight reductions) to install, were the overriding factors in favor of titanium in this study.[18]

Titanium has been selected for firemain piping on the new LPD class naval ship. This represents the first time titanium pipe has been designed into a new navy vessel. This occurred due to the success of titanium tubed heating & cooling systems onboard navy vessels for many years, as well as the competitive pricing of well engineered titanium piping systems.[21] In addition, the navy is considering titanium and titanium alloys for numerous other surface ship and submarine applications.

Fasteners

High strength titanium alloys are also being considered for use as fasteners for both navy and offshore applications.[22,23] Corrosion resistance and reduced maintenance costs are the primary incentives for looking at titanium. It has demonstrated complete resistance to SCC and hydrogen damage, which plague current fastener materials. Grades 21, 23, and 32 are being considered.

SUMMARY

The excellent corrosion resistance of titanium has always been at the fore of new applications for the metal. That becomes self evident when one sees all the engineering and design effort that has been put forth to overcome obstacles other than corrosion like welding, fabrication, fatigue, and lower cost manufacturing methods. These efforts have led to successful utilization of the metal, which once used, quickly becomes the new standard material for the application. Titanium is recognized as a technically correct metal for sea water and will enjoy enhanced and expanded roles in marine, naval, and offshore oil & gas production systems in the next few years. It can, with confidence, be specified into designs requiring 30-50+ years service life. Titanium is truly coming of age and assuming its role as a cost effective, environmental and maintenance friendly engineering material.

REFERENCES

1. J.A. McMaster, "Selection of Titanium for Petroleum Refinery Components", *Materials Performance*, NACE-International, Houston, TX, Vol. 18, No. 4, April, 1979, pp. 28-34.

2. J.R. Strickland, "Titanium Heat Exchangers Can Be Worth Their Cost to Cut Downtime", Oil & Gas Journal Reprint, Petroleum Publishing Company, September 6, 1976.

3. L. Lunde and H.B. Nordvik, "North Sea Applications of Titanium", Non-Aerospace Applications of Titanium, F.H. Froes, et. al., Eds., The Minerals, Metals & Materials Society, Warrendale, PA, 1998, pp. 173-180.

4. Titanium Offshore-A Designers and Users Handbook, Publication of TIG-The Titanium Information Group and The Titanium Technology Forum of IFE-Institutt for Energiteknikk, January, 1996.

5. R. Schutz, D.E. Thomas, "Corrosion of Titanium and Titanium Alloys," in J.R. Davis, ed., Metals Handbook, 9th Edition, Vol. 13, ASM, Metals Park, OH, 1987, pp. 669-706.

6. J.S. Grauman, "Titanium-Properties and Applications for the Chemical process Industries," in J.J. McKetta, ed., Encyclopedia of Chemical Processing and Design, Marcel Dekker, New York, Vol. 58, 1998, pp.123-147.

7. *Corrosion Resistance of Titanium*, TIMET Brochure, Titanium Metals Corporation, Denver, CO, 1997.

8. R.W. Schutz, J.M. Horrigan, and T.A. Bednarowicz, "Stress Corrosion Behavior of Ru-Enhanced Alpha-Beta Titanium Alloys in Methanol Solutions", Paper No. 261, CORROSION 98, NACE-International Annual Conference, Houston, TX, 1998.

9. G.J. Danek, Jr., "The Effect of Sea-Water Velocity on the Corrosion Behavior of Metals", *Naval Engineers Journal*, Vol. 78, No. 5, October, 1966, pp. 763-769.

10. R.P. Lee, "Special Corrosion Testing Methods", *Materials Performance*, NACE-International, Houston, TX, July, 1976, pp. 26-32.

11. F.W. Jessen and R.J. Molina, "Use of Titanium in Equipment Used in Certain Phases of Oil Production", Presented at 17th Annual Conference, March, 1961, Buffalo, NY, NACE-International, Houston, TX.

12. R.W. Schutz, "Understanding and Preventing Crevice Corrosion of Titanium Alloys", Paper No. 162, CORROSION 91, NACE-International, Houston, TX, 1991.

13. J.A. Davis and G.A. Gehring, Jr., "The Effect of Velocity on the Sea Water Corrosion Behavior of High Performance Ship Materials", *Materials Performance*, NACE-International, Houston, TX, April, 1975, pp. 32-39.

14. The Electrical Isolation of Cathodically Protected Pipelines, NACE Standard RP0286-86, NACE-International, Houston, TX, March, 1986.

15. R.D. Tems, "The Use of Titanium for Renovation of Ballast Water Systems on Three Gravity-Based Platforms", Presented at the International Conference on Titanium in Practical Applications, Norwegian Association of Corrosion Engineers, Trondheim, Norway, June, 1990.

16. G. Venkataraman and A.D. Goolsby, "Hydrogen Embrittlement in Titanium Alloys from Cathodic Polarization in Offshore Environments, and Its Mitigation", Paper No. 554, CORROSION 96, NACE-International Annual Conference, Houston, TX, 1996.

17. J.S. Grauman, "Titanium and Titanium Alloy Environmental Behavior Aspects for Application to Offshore Oil & Gas Production", Presented at Titanium Risers and Flowlines Seminar, SINTEF, Trondheim, Norway, February, 1999.

18. L. Lunde, D.K. Peacock, J. Murali, and R Aarnes, "Titanium Components in Offshore Gas/Oil Environments", Titanium '95: Science and Technology, Eighth World Conference on Titanium, P.A. Blenkinsop, et. al., Eds., The Institute of Materials, London, 1996, pp. 1711-1718.

19. J.S. Grauman and B. Willey, "Shedding New Light on Titanium in CPI Construction", *Chemical Engineering*, McGraw-Hill, New York, August, 1998, pp. 106-111.

20. D.K. Peacock and J. Skauge, "Titanium Pipe Demonstrates High Temperature Safety", Reprint from MBM-Metal Bulletin Monthly, Metal Bulletin plc, London, April, 1992.

21. J.A. Mountford and J.S. Grauman, "Titanium for Marine Applications," presented at the 2nd *Corrosion Control Workshop*, sponsored by the Colorado School of Mines, New Orleans, LA, Feb. 1997.

22. J.S. Grauman and D.K. Peacock, "Performance of a High Strength Beta Titanium Alloy Under Tensile Load with Cathodic Charging of Hydrogen", Titanium '95: Science and Technology, Eighth World Conference on Titanium, P.A. Blenkinsop, et. al., Eds., The Institute of Materials, London, 1996, pp. 1844-1851.

23. R.L. Tregoning, D.M. Aylor, and I.L. Caplan, "High Strength Titanium Alloys for Naval Fastener Applications", Titanium '95: Science and Technology, Eighth World Conference on Titanium, P.A. Blenkinsop, et. al., Eds., The Institute of Materials, London, 1996, pp. 1726-1733.

Composite Material Offshore Corrosion Solutions

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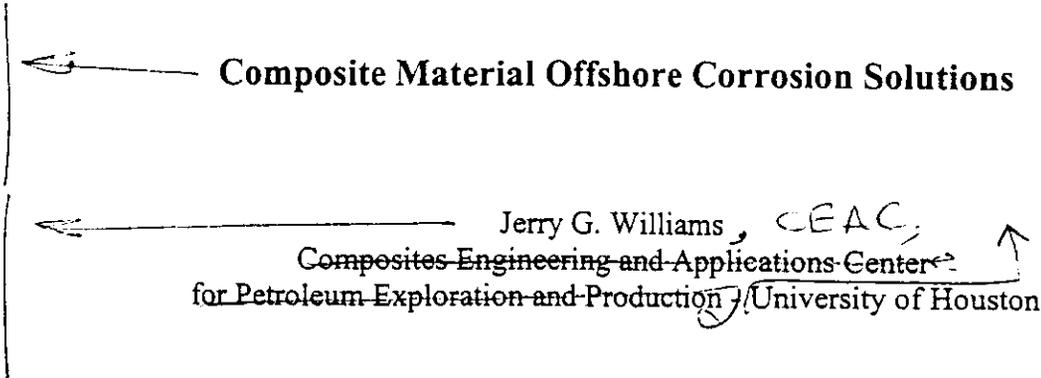
ABSTRACT

Corrosion and weight control are the two main factors motivating the interest and growth of the use of composite components in offshore oil and gas exploration and production operations. Controlling and inhibiting corrosion and periodic replacement of metal components costs the oil industry large amounts of money. Composite materials can usually be chosen which will resist corrosion and be compatible with the chemicals used downhole and offshore. Reducing the weight of deep and ultra deepwater floating platforms has become a high priority and low density composites yields the most effective solution. Oil and composite suppliers efforts, in part complemented by government support in the United States and Europe, have encouraged a slow but growing acceptance of the use of composites in offshore operations. Safety critical components such as fire water piping as well as secondary structure including gratings, handrails and stairs constructed of fiberglass and polymeric resin are now routinely specified for deepwater platforms. Significant advancements have been made in the materials (i.e., fire resistant phenolic resin) and in the design and fabrication methods used to address safety issues and to improve performance and reliability. More structurally demanding applications such as a high pressure riser tensioner accumulator vessels constructed of carbon and glass fibers have also been introduced offshore. Hybrid construction combining different materials to achieve the required structural performance while minimizing cost is another benefit derived from the design flexibility inherent with composites. This paper provides an overview of components currently used on offshore platforms and highlights proposed advanced applications under development.

INTRODUCTION

Properly designed, composite structures offer the potential to reduce maintenance costs, save weight, enhance safety, reduce adverse environmental impact, improve durability, and provide enabling capabilities. Some of the advantages offered by composite materials are listed below.

Some applications capture several of the advantages of composites making composites a clearly superior choice while other applications, for cost or special performance reasons, are better served using metals. The choice of materials has broadened and new developments will continue to offer even more options. Corrosion resistance and the associated cost savings provide good incentive for deployment of composites onshore as wells as offshore. Weight savings, however, are more valuable in deepwater offshore operations where light-weight components create synergistic benefits through downsizing of supporting structures and systems.[1-5] High strength or stiffness is the most important consideration for some applications while special properties such as electromagnetic transparency or low thermal conductivity may be important drivers for other applications. The use of composites also allows for greater design flexibility by allowing mechanical and physical properties to be tailored to meet specific design requirements and to provide improved cost-effective system solutions. On a one-on-one replacement basis, composite components can be less expensive than metals while other applications require life cycle costs be considered to capture cost savings. Advanced composite components constructed using higher cost carbon fiber are usually (but not always) more expensive than their steel counterpart. Weight and cost savings for the associated support structure and systems, however, can frequently shift the cost differential and make the integrated composite system solution less expensive. In addition, the economic incentive to use composite components can often be demonstrated based on their capability to improve performance and reduce life cycle costs.

BENEFICIAL CHARACTERISTICS OF COMPOSITES

- Corrosion and Chemical Resistance
- Light Weight
- High Strength and Stiffness
- Fatigue Resistance
- Low Thermal Conductivity
- Low Electrical Conductivity
- Electromagnetic Transparency
- Easy to Install (Handle/Cut/Mill, etc.)
- Low Flow Friction and Wear
- Design Flexibility
- Integration of Electrical and Information
  Transmitters Into the Laminate Walls
  for Protection and Structural Monitoring

Over the last ten years composite have been accepted in the offshore oil industry for applications previously reserved for metals. Composite materials provide many desirable properties including those listed above, however, the two most common reasons to use composite materials in the oilfield are to avoid corrosion and to save weight. Illustrations of corrosion of steel pipe and gratings are shown in Figure 1.

(a) Steel pipe corrosion.
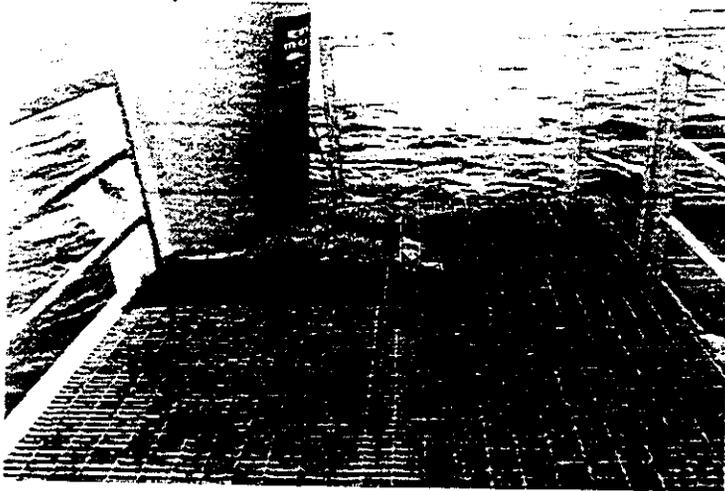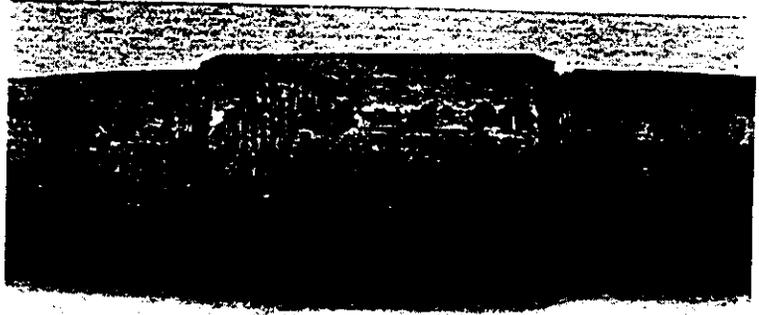
(b) Steel grating corrosion.

Figure 1.- Corrosion control is a major reason FRP is being used offshore.

Structural applications for a platform may be classified according to load range as heavily loaded (i.e., tendons, risers, and high-pressure piping), moderately loaded (i.e., helideck, flare tower, and low-pressure pipes and vessels), and secondary structure (i.e., gratings, ladders, ducts, and living quarters). The higher the load category, the less prepared is the state of the technology for near-term application. Another convenient way to categorize oil industry applications in the marine environment is by function or location as presented below.

COMPOSITE APPLICATION CATEGORIES

1. Platform to Sea Bed (tethers, riser, mooring rope, etc.).
2. Processing Facilities (containers, separators, pumps, etc.).
3. Topside Secondary Structure (grating, hand rail, etc.).
4. Housing & Protective Structures (accommodations, walls, etc.).
5. Topside Piping (Waste water, firewater, sea water, potable water, drains, etc.).
6. Tanks & Pressure Vessels (storage vessels, tanks, pressure accumulators, etc.).
7. Platform Structure (helideck, primary deck, hull, column, pontoons, etc.).
8. Downhole (coiled tubing, drill pipe, tools, sensors, etc.).
9. Subsea (umbilical, injection and flow lines, protection, etc.).
10. Ship Applications (pipe, containers, walls, mast, doors, pumps, etc.).

Deepwater oil and gas resources offer significant potential for development, particularly in the Gulf of Mexico, Brazil, West Coast of Africa and other deepwater basins around the world. Major oil companies, composite product manufacturers, oil service companies, and regulatory agencies have worked together over the last ten years in a low-key, but concentrated effort to advance composites technology and make composites a viable option for oil industry applications.[6] The technology has advanced and lightly-loaded secondary structures such as low-pressure fiberglass piping, gratings, and secondary structure are now routinely used offshore. Longer range, new composite applications are being developed to meet demanding structural performance requirements such as production and drilling risers, spoolable pipe, and high-pressure vessels. The highest payoff potential for composites is in deepwater associated with heavily-loaded, weight-sensitive applications where metal designs become impractical or extremely expense. Low-cost manufacturing processes and innovative hybrid designs which blind different materials such as glass and carbon are important factors in helping make composites affordable and competitive with metal designs. In support of these applications, qualification guidelines have been prepared to insure their quality and performance. Some applications in service, such as firewater ring main and deluge pipe, are extremely safety critical and demanding tests and guidelines have been specified to insure their safe performance. Recent depressed oil prices have delayed some offshore developments, but new discoveries are being made and when deepwater projects resume, composites are expected to play an increasingly important role in providing improved performance and helping make the cost of offshore development affordable. The present paper presents a review of existing and new composite technology being deployed and developed for the oil industry.

COMPOSITE MATERIALS BACKGROUND

Composite materials as used in this report consist of small diameter fibers of high strength and modulus embedded in a polymeric matrix. The fibers are the main load-carrying member while the matrix maintains the fibers in the desired orientation, acts to transfer load into the fibers and protects them from the surrounding environment. The most common fibers are glass, carbon and aramid supplied on spools such as shown in Figure 2. Other fibers such as silicon carbide, boron and aluminum oxide may have superior properties, but, are normally not used because of higher cost.

The polymeric matrix materials are classified as either thermoset or thermoplastic. The most common polymeric matrix materials are polyester, vinyl ester, phenolic, and epoxy. Fibers are incorporated in the matrix in long continuous lengths or are sometimes utilized as short discontinuous fibers. Structural composite components are normally formed by stacking several lamina (individual plies) to build up a composite structural laminate.

Fibers

A large number of fibers with different physical and chemical properties are commercially available. They can be obtained in several different physical forms including tow, ribbon, continuous woven mats and chopped strand mats. Fiber tow is the most common form used for high performance reinforcement. The fibers most likely to be used in the offshore industry are E and S glass, carbon and aramid. Table I provides an overview comparison of these fibers. Other fibers such as polyester and polyethylene are being used or considered in pure fiber form

(without resin) for mooring ropes, but they are not expected to be competitive in composite form (with resin) due to their significantly lower modulus.
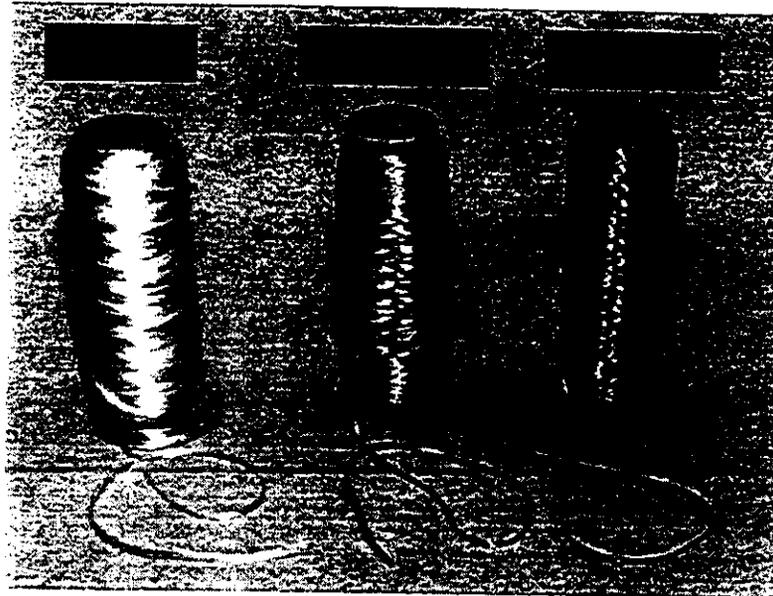
Figure 2.- Primary fibers used in construction of composites.

TABLE I.- QUALITATIVE COMPARISONS BETWEEN DIFFERENT CLASSES OF FIBERS.

Fiber	Advantages	Concerns
E-glass	Low cost	Moisture degradation
Carbon	High specific strength/stiffness Good fatigue and creep resistance	Higher cost Damage tolerance
Aramid	High specific tensile strength/stiffness Good damage tolerance	Low compressive properties High moisture absorption Difficult to machine

Resins

Resin selection requires consideration of properties (chemical resistance, toughness, abrasion resistance, stiffness, and strength), processing (lay-down rates, process temperature, and processability), and cost (materials and processing). Thermoset resins are more commonly used to make composites for oil industry applications than thermoplastic material. Epoxy, phenolic, vinyl ester, and polyester are the most commonly used thermoset resins. A wide variety of commercial thermoplastics are available. These include polyamide (PA - nylon), polyamide-imide (PAI), polyimide (PI), polyarylate (PAR), polyaryl sulfone (PAS), ployether sulfone

(PES), polyphenylene sulfide (PPS), high density polyethylene (HDPE), polyethylene terephthalate (PET), polyetheretherketone (PEEK) and polyetherketoneketone(PEKK). Thermoplastic resins are attractive because they offer good mechanical properties, exhibit excellent toughness and damage tolerance, display process repeatability, and simplify repair. Since thermoplastics have limited cross-link density, they typically exhibit lower chemical and creep resistance. Chemical resistance, however, can be improved by the development of crystalline morphology or by achieving active polymer linkages. Thermoplastic resins with an acceptable upper temperature range are usually more expensive than comparable temperature use thermoset resins.

Environmental Effects

In general, the fundamental mechanisms of corrosion are different for composites and metals. The lack of corrosion in the classical sense is one of the primary assets of composites. In most cases, metals are attached at the surface by electrochemical processes. Material degradation by diffusion of the material into the metal is not very common, with a few exceptions such as the process of hydrogen embrittlement of steel. Diffusion of material into a plastic material, however, is quite common and the effect ranges from negligible to catastrophic such as the dissolving of the plastic by certain solvents. The process may or may not involve a chemical reaction. For example, absorption of water does not usually involve a chemical reaction. To varying degrees for different polymers, water absorption can change the physical properties of the material such as lower the glass transition temperature, reduce the stiffness, and increase the sensitivity to creep. In addition, moisture and chemicals may attack the interface between the fiber and the resin. Carbon and glass fibers are relatively insensitive to the environment, except the strength of glass fibers can be reduced by water. A sizing coating applied during manufacture is used to protect glass fibers.

As with metals, not all polymers behave the same with regard to environmental exposure. In fact, the diversity of polymer properties allows the selection of a resin in most cases which will be compatible with most of the chemicals and environments experienced in the oil industry including alkalines, acids, caustic solutions, solvents, oxidizing agents, and moisture. Some resins also have superior resistance to high temperatures, tolerance to ultraviolet radiation and good performance in a fire. Phenolic resins, for example, perform well in a fire and emit low smoke or toxic decomposition components. Polyimide and some thermoplastic resins perform well at high temperatures, but are usually much more expensive than epoxy or vinyl ester.

Composite materials also exhibit certain limitations in performance. They are usually more susceptible to impact damage than metals and this must be factored into the design of components. Carbon fibers can also present a galvanic problem when they are joined to certain metals. Being at the cathodic end of the electromotive series, carbon fibers act as a noble metal being impervious to corrosion itself, but they accelerate corrosion in the adjacent less noble metal. Aluminum is more sensitivity to galvanic corrosion than steel and titanium is less sensitive than steel. Carbon fiber is compatible with some metals such as austenitic stainless steel, superalloys such as A286 and Inconel 718.[7] In making bolted joints, it is advisable to isolate the metal bolt from the composite using a sealant. Other precautions include coating cut and exposed surfaces. In bonded joints between metal and carbon, the primary protection against

galvanic corrosion is the adhesive. Composite materials with glass or aramid fiber reinforcement do not present a galvanic corrosion issue.

Manufacturing

Assuming the application selected has merit, affordable composite structures depend on using a low-cost manufacturing process. In general, this implies that the manufacturing process be automated (not hand layup) and that glass fibers will be used if their properties are adequate. Hybrid construction incorporating combinations of glass and carbon or other fibers allows greater flexibility in reducing weight and meeting structural requirements while also paying close attention to the cost of raw materials. In aerospace, most composite components are made using prepreg tape in which the resin is put onto fiber bundles in a separate process. This improves the quality control, but adds significant cost to manufacturing. Preferred processes to reduce cost involve combining the resin and fiber at the point of application such as filament winding or placing the fiber into the part in a dry form and drawing the resin into the fiber.

Low cost manufacturing processes include filament winding, pultrusion, vacuum resin transfer molding (VRTM), and resin transfer molding (RTM). Sometimes it is necessary to use preform material such as stitched or braided material, but in general, the lowest cost process involves applying resin to fiber applied in roving form during the manufacturing process. If the application involves exposure to elevated temperature, the resin must be cured at a temperature higher than the application temperature. Most tubulars are constructed using filament winding while non-symmetric shapes can be pultruded. The critical parameters for making quality components are fiber wet-out, precision fiber orientation, and resin flow/consolidation and solidification.

CURRENT OFFSHORE COMPOSITE APPLICATIONS

Fiberglass Reinforced Plastic (FRP) Offshore Applications

Filament wound fiberglass pipe was first introduced into the oil field in the late 1950's. The lighter weight, fatigue and corrosion resistance and associated low life cycle costs make FRP components very attractive for expanded offshore applications. FRP components are from one-third to one-fifth as heavy as equivalent steel components and the lighter weight permits FRP products to be more easily handled and installed. FRP connections eliminate the hazards associated with welding and the experience level required to make quality bonded connections can be learned very quickly. The net result is that FRP composites can provide significant cost savings relative to metal.

There has been significant use offshore of FRP in the last five years in the Gulf of Mexico, Middle East, Far East, Africa and the North Sea. FRP pipe, however, has been used offshore for over twenty-five years. An example is the low pressure pipe used in Dubai in the water injection system with pipe ranging in size up to 36-inch in diameter as shown in Figure 3. In addition, FRP firewater pipe was used to replace steel pipe on all of the platforms in the Dubai Southwest Fatah field. In recent years, significant quantities of FRP have begun to be introduced into

operations in the Norwegian sector of the North Sea including applications on Valhal,[8] Ekofisk, Ula, Statfjord, Gullfaks, Draugen, Troll and Heidrun. Environmental concerns also encourage the use of composites. An emerging design philosophy is to use non-corrosive composites to permit elimination of chemicals such as corrosion inhibitors required to protect steel pipe.
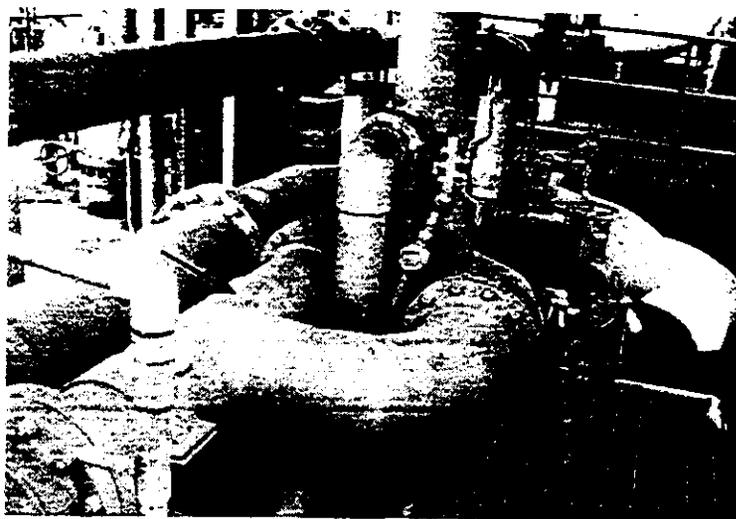
Figure 3.- FRP pipe installed on offshore platform in Dubai.

The total installed cost of fiberglass piping systems is on the same order as carbon steel and less than high performance alloys and copper nickel as shown in the Table II comparison of relative installed cost. The cost advantage for fiberglass pipe is most significant for large-diameter pipe and for complex installations since the higher cost for fiberglass pipe is offset by the lower labor costs of installation. Fiberglass tees and elbows can be installed in approximately 40% of the time required for the corresponding steel fittings. Fiberglass pipe carries a material cost premium of about 30% in 2-inch diameter, is approximately equivalent in price for 3- and 4-inch sizes, and is less expensive than Schedule 40 galvanized steel in the larger diameters decreasing to about one-half the cost for 12-inch pipe. In contrast, fiberglass fittings are generally 2 to 3 times more expensive in the smaller diameters, but cost about the same or less in the larger sizes.

TABLE II. - NORWAY, OFFSHORE INSTALLED PIPE COST COMPARISON.

Material	Relative Cost
Carbon Steel	1.0
FRP	1.0
316 Stainless Steel	2.2
CuNi	3.5

Much of the success in getting approval for FRP applications on platforms has been the result of focused R&D programs designed to advance the technology and to address specific issues of concern to the operators and regulatory authorities. Interaction of industry task groups with the NPD in Norway,[9] HSE in the U.K.,[10] and the MMS and Coast Guard in the United States is leading to the development of specifications and guidelines. Availability of industry accepted guidelines has been identified as one of the factors which will help make composite materials a viable option and permit selection based on performance and economics rather than prescriptive rules which favor metals.

Topside Applications of FRP in Gulf of Mexico (GOM)

Recent vintage deepwater Gulf of Mexico (GOM) platforms have made liberal use of FRP pipe to transport low pressure water and FRP grating.[11] In addition, secondary structural elements such as hand rails, framing, low-pressure tanks, etc. are also being used. This section provides representative examples of offshore composite applications.

A dockside view of the Marlin platform during construction is shown if Figure 4. The pipe suspended from the bottom of the platform with a U-shaped bend at the lower left is the firewater ring main constructed of glass fiber and polysiloxane-phenolix resin. The FRP deluge firewater pipe on the Marlin TLP shown in Figure 5 is qualified to resist a jet fire. A photograph showing FRP pipe used for seawater transport on the Ram Powell platform is shown in Figure 6. The use of FRP pipe for the firewater and seawater handling on the Mars TLP platform provided weight savings of approximately 80 tons. The FRP firewater ring main and deluge pipe used on recent GOM TLPs meet United States Coast Guard criteria defined in Policy File Memorandum PFM 1-98 16714.
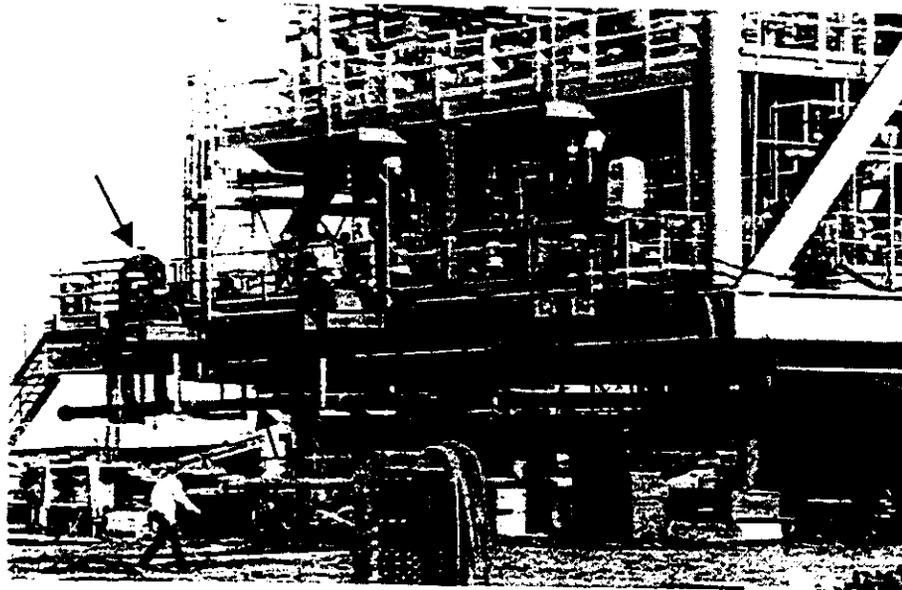
Figure 4.- FRP firewater ring main used on GOM platform. (Ameron)
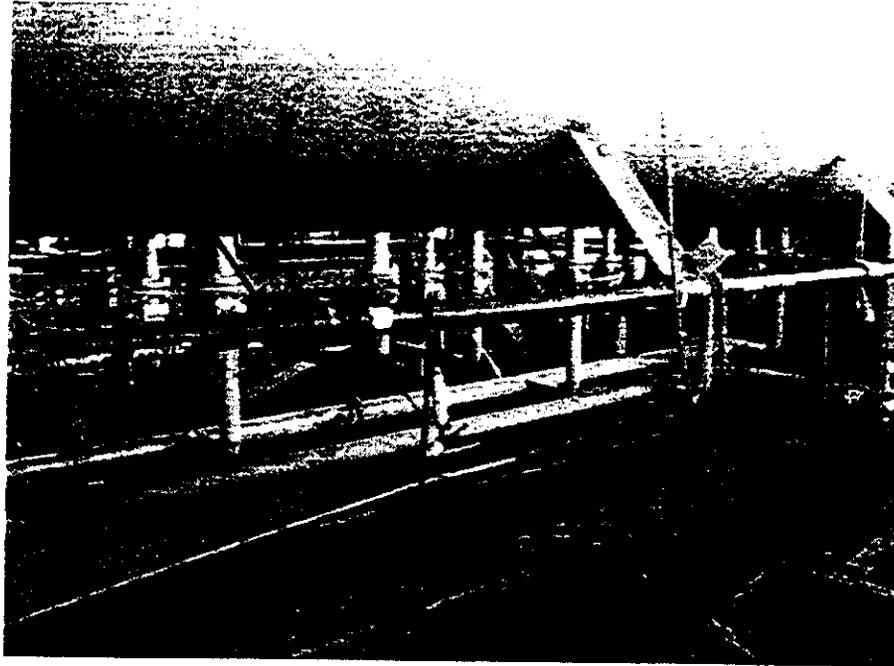
Figure 5.- FRP firewater deluge pipe. (Ameron)
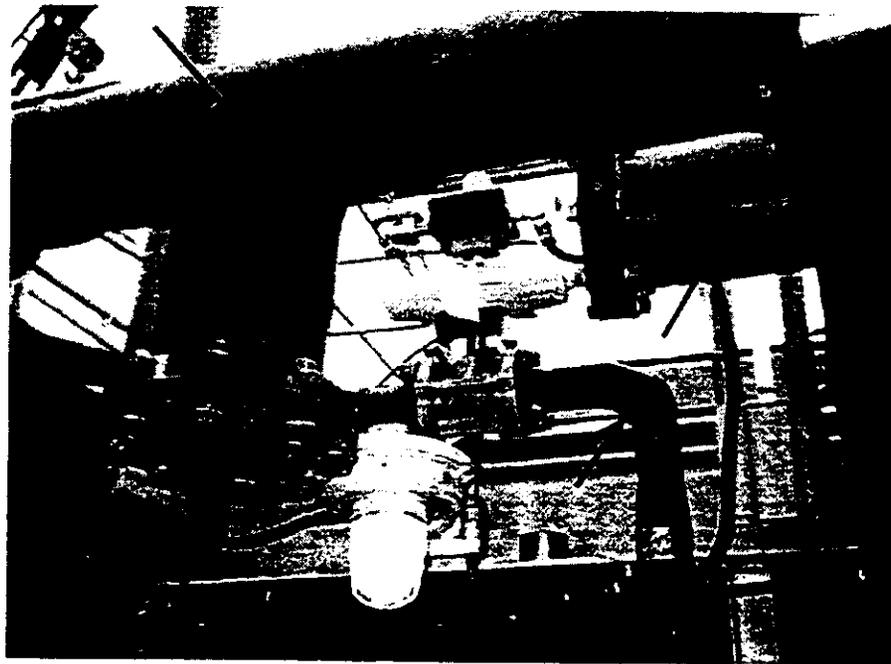
Figure 6.- FRP pipe used for transporting seawater on GOM platform. (Specialty Plastics)

The FRP grating shown in Figure 7 is constructed of pultruded glass fiber and phenolic resin to provide a more fire resistant product. Over 500,000 square feet of phenolic grating has been used on recent TLP platforms installed in the Gulf of Mexico. Weight savings of approximately 66 percent are provided by the FRP gratings compared to steel while the installed cost is approximately equal. Long term savings can be expected based on life cycle costs and reduced maintenance. Other benefits of the FRP grating is that shut-down due to hot work is not required during modifications and light-weight characteristics make handling easier. FRP gratings are also easier to walk and kneel on and have excellent anti-skid characteristics. The Strongwell FRP phenolic gratings pass rigid fire safety tests as defined in United States Coast Guard Policy File Memorandum PFM 2-98 9078.
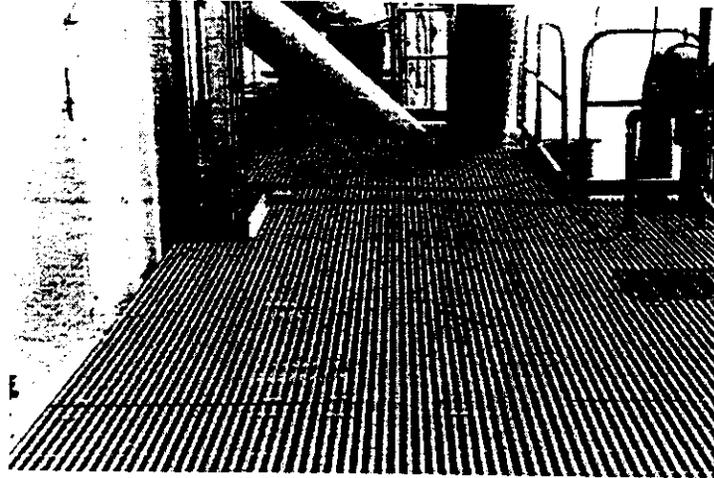
Figure 7.- FRP grating on GOM platform fabricated using fire resistant phenolic. (Strongwell)

A photograph showing FRP cable trays and secondary structure installed on Gulf of Mexico platforms is presented in Figure 8.
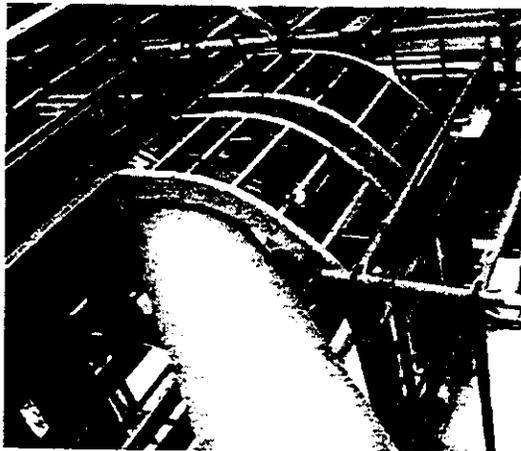
(a) FRP Cable Tray

(b) FRP secondary structure

Figure 8.- FRP cable tray and secondary frame structure used on GOM platform.

Composites on Small Unmanned Platforms

Many offshore oil and gas discoveries are small reservoirs in which the production rate does not justify the construction of a large supporting platform. To develop these reservoirs, small unmanned platforms are increasingly being used. Minimum facilities and accommodations are available and emphasis is placed on reducing the requirement for maintenance. An example is the Amoco Davy and Bessemer single leg mono-tower platform concept shown in Figure 9 which made liberal use of composites[12]. The platform is not normally manned and is designed for removal, refurbishment and re-installation at new locations making it sensitive to topside weight. Amoco identified the Davy and Bessemer topsides facilities as good applications for FRP materials because of the combined benefits of weight savings and corrosion resistance. The extensive range of composite material applications resulted in more than 100 tonnes weight saving for the 400 tonne topside. The FRP applications installed on Davy and Bessemer include: office, equipment room, tool room, handrails, ladders on topsides and on columns, gratings, fuel loading arm, drain pipe, caissons, diesel tank, lube tank and water utility tanks. Gratings and modules were made using phenolic resin to provide the required fire resistance. The handrails were manufactured using class 1 polyester resin. All other application were made using polyester resin except the caisson and drain pipe which used epoxy resin. The use of FRP for major structural beams and the helideck were attractive in terms of potential weight savings, but the time scale for design was too short for this to be an available option. Amoco studies indicate that there was no significant cost or weight advantage to using composite cable tray versus stainless steel trays.
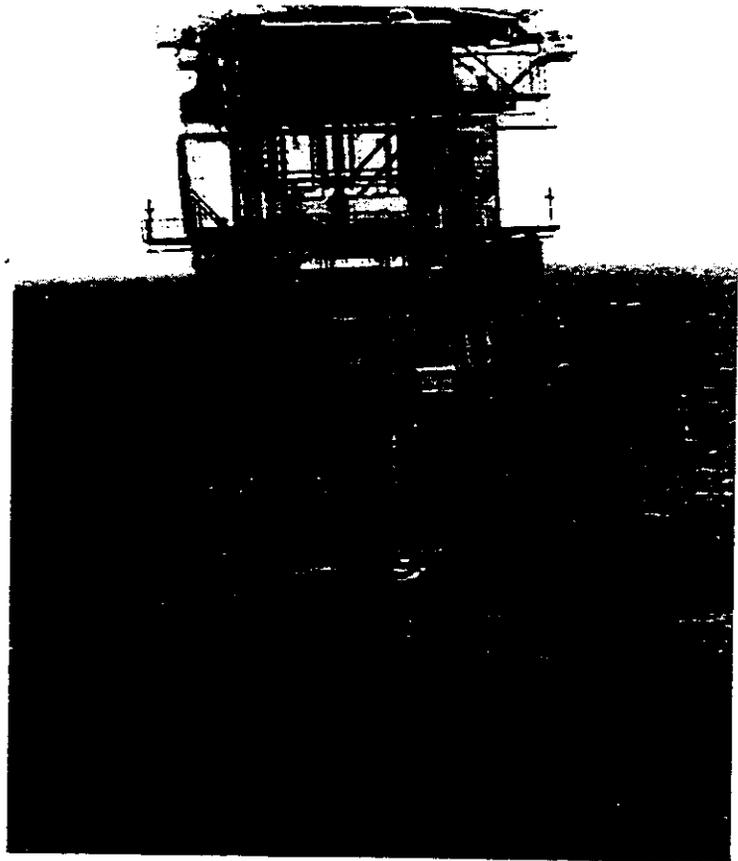
Figure 9.- Davy/Bessemer class of mono-tower platform designed for minimum maintenance.

POTENTIAL NEW OFFSHORE COMPOSITE APPLICATIONS

As the oil industry moves to explore and development ultra-deepwater reservoirs, weight and performance of critical systems become increasingly important. Some of the platform configurations used offshore are illustrated on Figure 10. The Tension Leg Platform has been the most widely used configuration for the 2000-ft to 4000-ft water depth, but recent studies seem to prefer the SPAR, particularly for water depths greater than around 3000-ft. TLP steel tendons become increasingly heavy at ultra deepwater depths due to the requirement to resist collapse of air filled tubulars. The applications with the highest return are those which provide a significant operational improvement such as extending the water depth of economical operation for a TLP or where reducing the weight of the component allows complementary weight saving in components and structures that support it. The riser is a good example of the latter because saving weight on the riser also saves weight on the deck structure and on the hull or buoyancy modules used to support it. For a TLP, saving weight on the riser also reduces the amount of pretension required on the tendons. Table III from reference 2 estimates the relative magnitude of the effect of selected components on other element of a TLP. In each case, the structural element being studied is given a relative value of 1. It can be seen for a TLP that saving weight on the topside payload and riser have the largest effect and saving weight on the hull has the lowest.
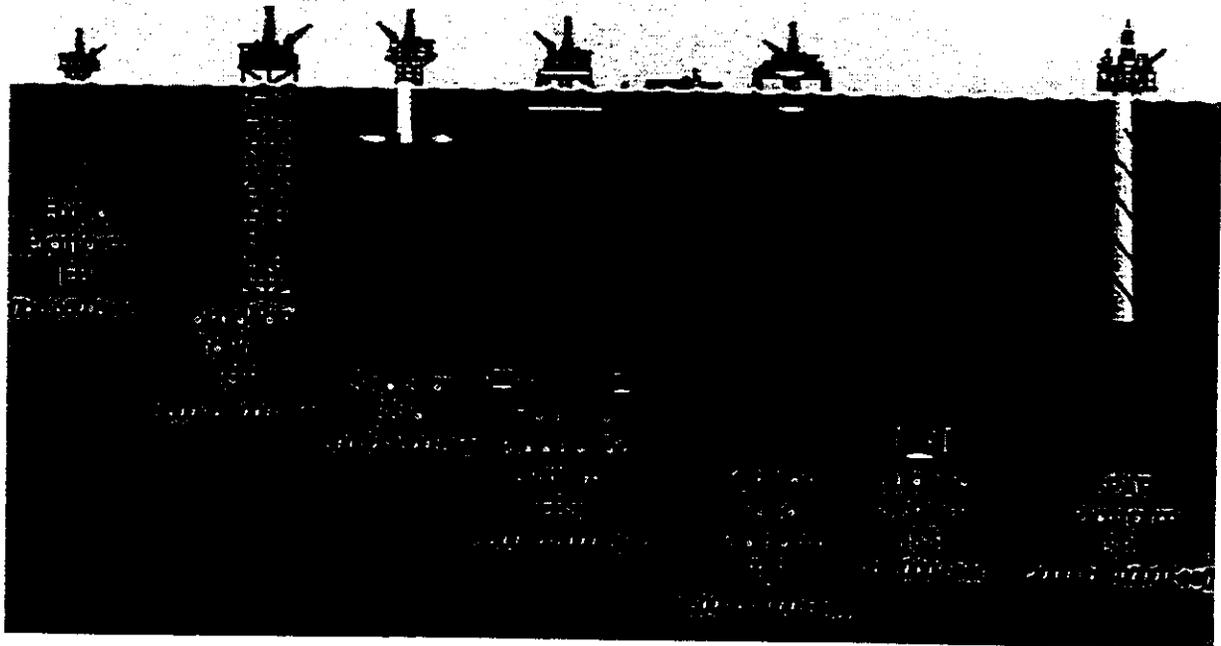
Figure 10.- Deepwater production platform configurations.

Table III.- TLP WEIGHT SAVINGS LEVERAGE.

Component	Hull (ton)	Deck (ton)	Payload (ton)	Riser (ton)	Tether Pretension (ton)	Total Savings (ton)
Hull	1.0	0	0	0	0.32	1.32
Deck	0.47	1.0	0	0	0.47	1.94
Payload	0.72	0.5	1.0	0	0.71	2.93
Riser	0.69	0.5	0	1.0	0.66	2.85

The remainder of this section highlights composite components currently being considered for deepwater platforms including the following applications.

- Production Risers
- Drilling Risers and Choke and Kill Lines
- Drill Pipe and Torque Tube Applications
- Buoyancy Modules
- Spoolable Pipe
- Platform Primary Structure
- Process Equipment / Pressure Vessels
- Accommodation Modules
- Tendon
- Synthetic Fiber Mooring Rope

Production Riser

A program to develop a composite riser was first initiated by Institut Francais du Petrole and Aerospatiale in 1985.[13-15] The program resulted in a successful prototype, but it was early in the deepwater development activity and the estimated cost was considered too expensive for the market. The drop in the cost of advanced composites and the accelerated pace of deepwater development in recent years renewed interest in a composite production riser. A joint industry project led by Lincoln Composites, in part supported by the National Institute of Standards and Technology (NIST) Advanced Technology Program (ATP), continued the composite riser development.[16] The 10.75-inch composite production riser is a hybrid construction composed of carbon and glass fibers embedded in an epoxy matrix. The composite body transfers load into a metal end coupling using a "trapped lock" design commonly used in the aerospace industry. The composite material is wound over and into a sculptured hill and valley profile in the metal which structurally links the composite body and metal coupling. Internal and external liners are incorporated to provide a fluid-tight barrier and protection from damage. The current design is suitable for water depths up to 5000 feet, but Lincoln Composites projects that a product can be designed to accommodate ultra deepwater requirements.

The NIST ATP production riser program involved an extensive test program with over sixty, 12 feet long specimens tested under different load conditions simulating the environment

experienced in service including internal and external pressure and axial tension and fatigue. The average burst pressure for 6 specimens was 11,635 psi and the average axial load at failure for 6 specimen was 942 kip.[17]

A photograph showing a 50-ft long section of production riser is shown in Figure 11. The weight of the riser in air is 1450 pounds which represents a 41 percent weight savings compared to steel. The corresponding weight savings in water is 68 percent. This weight savings provides a significant impact on the platform design considering the long length from the platform to the sea bed and the large number of risers deployed a typical deepwater platform.

Figure 11.- Composite production riser. (Lincoln Composites)

Drilling Risers and Choke and Kill Lines

Two efforts are currently actively engaged in developing a composite drilling riser. One effort led by Northrop Grumman Marine Systems and ABB Vetco Gray is co-sponsored by NIST ATP.[18] The design requirements include 3000 psi operating pressure and 1.5 million pounds axial load. The drilling riser is constructed of carbon fiber and epoxy. Metal end fittings with a sculptured upset are over wound during the process of making the tube composite body and welded to a metal threaded end coupling. A 22-inch diameter prototype fabricated in this program is shown in Figure 12. Over 50% weight savings are projected for the composite drilling riser. The sponsors indicate plans to test the prototype in deepwater operations in Brazil. Northrop Gurmman Marine Systems and ABB Vetco Gray are also developing a composite choke and kill line.
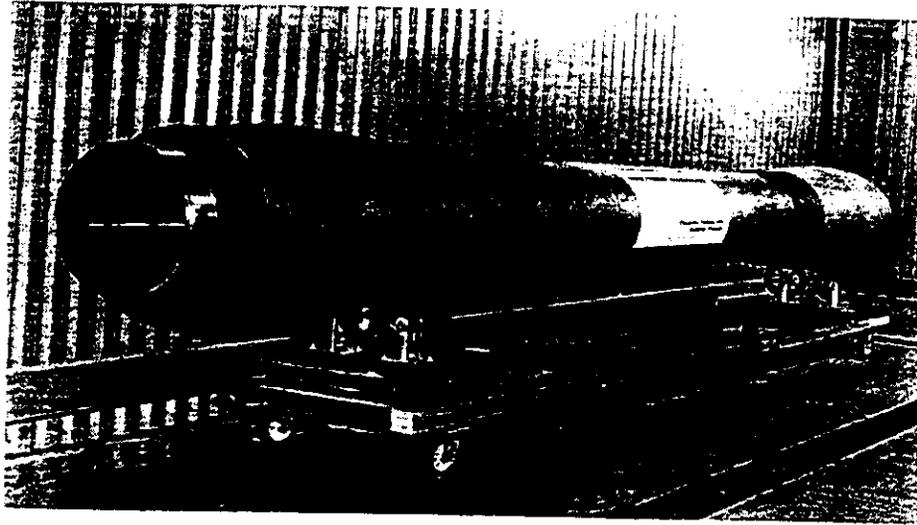
Figure 12.- Composite drilling riser.
(Northrop Grumman Marine Systems and ABB Vetco Gray)

The second effort to develop a high pressure composite drilling riser[19] is being led by Conoco Inc. and Kvæmer with fabrication of the component by Lincoln Composites. The program plans include field testing sections of 48-ft long, 22-inch diameter composite drilling riser on the Heidrun TLP in the North Sea. The design is constrained to be compatible with properties characteristic of the current titanium drilling riser. The requirements for the drilling riser are more demanding than for the production riser. Not only is the diameter much larger, but large bending loads are imposed. Also, the impact load criterion imposed for the Norway application includes a 250 kJ energy impact requirement for dropped objects.

Drill Pipe and Torque Tube Applications

The properties of composites also provide good engineering solutions for applications in which torque is a significant design load requirement. Several programs have studied the use of composites for drill pipe and torque shaft applications. AEA Petroleum Services in the United Kingdom sponsored a JIP on composite drill pipe and composite drill pipe was the focus of a NIST ATP program led by Spyrotech. Composite coiled tubing is also being considered for use as drill pipe to transport the mud motor downhole and to supply the mud to drive the motor.

In another torque application, a mud motor composite torque shaft was designed, fabricated and tested by Conoco and DuPont in the late 1980's. The problem addressed was to prolong the life of the universal joint in the mud motor which at the time of the development was the major weak link in the mud motor assembly. The design used carbon fiber and a PEEK thermoplastic resin. Test specimens were successfully laboratory tested in a dynamometer under representative field conditions including bending, compression, and torsion. The composite mud motor torque shaft is shown during assembly into the mud motor in Figure 13. Although the shaft passed dynamometer tests with loads higher than the design loads, it failed during a subsequent field test. It was believed the tube was

damaged during the field make-up of the mud motor assembly when larger loads were imposed than the shaft was designed to carry. The development of the composite torque shaft was dropped when mud motor manufacturers developed alternative solutions to the shaft failure problem.
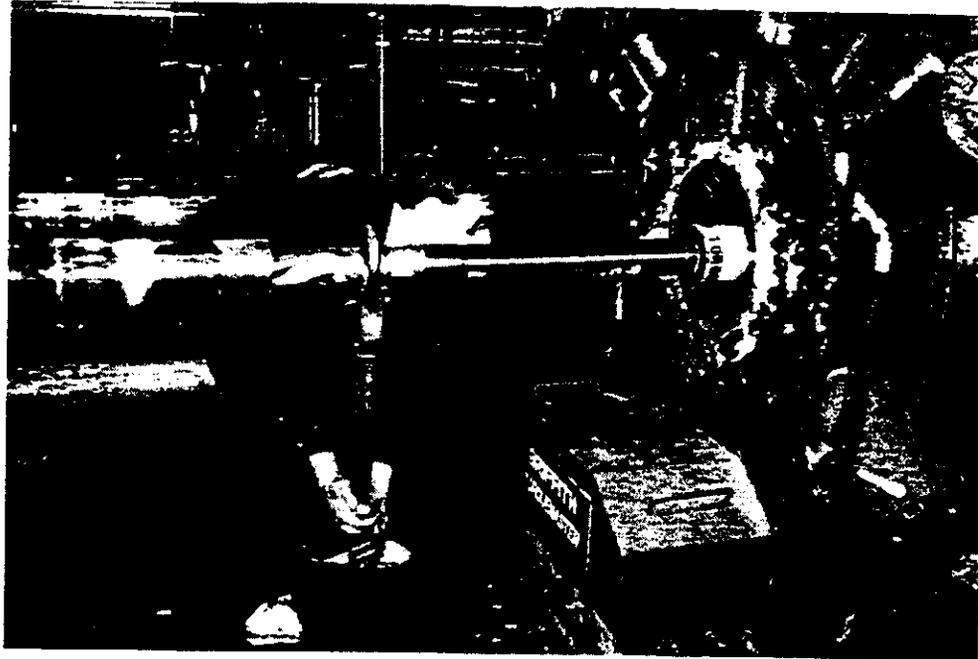
Figure 13.- Composite mud motor torque shaft (Conoco and DuPont).

Composite Buoyancy Vessels

There are many applications in the offshore oil industry requiring buoyancy to support the weight of submerged components, i.e., drilling risers, production risers, and mooring lines. Buoyancy modules are currently made from syntactic foam or are pressure vessels constructed of steel. To prevent collapse due to the ocean hydrostatic pressure, the density of the syntactic foam increases significantly as a function of water depth. Large light-weight composite pressure vessels with integral bulkheads and stiffening may be able to compete with syntactic foam and steel vessels on the basis of cost per pound of buoyancy. Filament winding, pultrusion and integrated assembly manufacturing processes offer the potential to make large-scale structures at competitive cost. A study to make the entire hull structure of a Tension Leg Platform from composites is described in reference 5. Innovative structural concepts and low-cost manufacturing processes will be critical in making composite buoyancy components competitive with metals.

Spoolable Pipe

A whole new class of products is being introduced into the oilfield based on a recently developed technology to design and fabricate very long lengths of pipe which can be bent to small radius of curvature for placement onto a cylindrical spool[20]. By tailoring the cross-section to optimally carry pressure, tension, compression and bending loads; it is possible to wind a high pressure composite pipe onto a relatively small-diameter spool. The composite pipe is tailor designed to be able to repeatedly experience large strains without failure. The basic concept for the pipe is illustrated in Figure 14. Several cross-ply laminates constructed of glass, carbon or aramid in an epoxy or other resin are wound onto a thermoplastic liner constructed of high density polyethylene, polyamid, PVDF or other material. Several companies worldwide are in the process of developing and introducing spoolable composite pipe products including Fiberspar Tubular Products Inc.,[21, 22] Compipe a/s,[23] Hydril Company,[24] Proflex Pipe Corporation,[25] and Tubes d'Aquitaine[26].

Structural Lamina (Epoxy with glass, aramid or carbon fiber)

Thermoplastic Liner (HDPE, PA, PVDF, etc.)
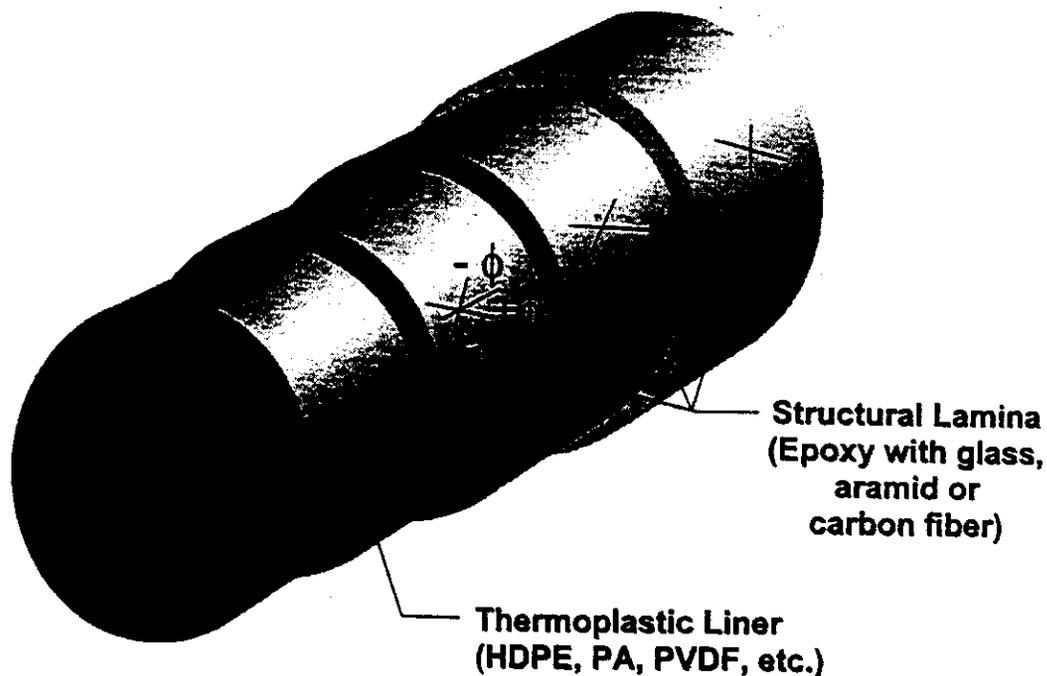
Figure 14.- Spoolable composite pipe with thermoplastic liner.

The process for making spoolable pipe is different from conventional filament winding in that instead of the pipe rotating to apply the fibers, small spools of fiber articulate around the pipe using ring winders or braiders such as illustrated in Figure 15. Several ring winders or braiders are placed in series and each apply a discrete layer to accumulate the required wall thickness. The speed of the winder and speed of translation of the pipe along the assembly line determine the cross-ply angle for each layer. Axial strains (bending plus axial loading) on the order of 2 percent can be applied if the cross-ply angle does not approach 0-degrees (axial).
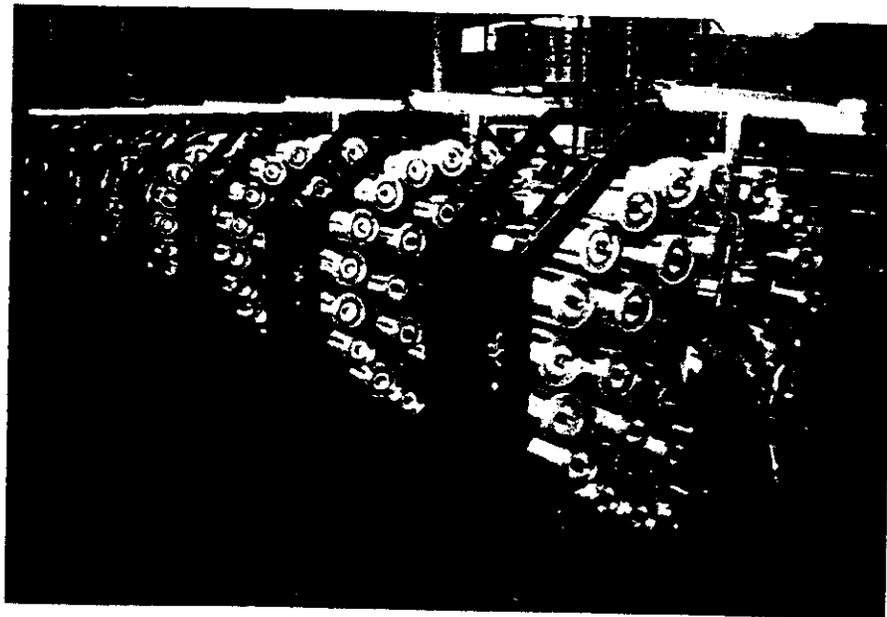
Figure 15.- Ring winders in series used to fabricate spoolable composite pipe.

Conoco conducted the early development work on spoolable pipe[20] and worked with Fiberspar Tubular Products in the United States and Compipe a/s in Norway to develop products. An early prototype of composite coiled tubing illustrating the bending capability is shown in Figure 16. The Conoco effort focused on developing a product which would meet the rigid requirements of the coiled tubing application. The primary advantage over steel coiled tubing is that the composite can be deployed repeatedly at higher pressures. Other advantages include the potential for longer reach in horizontal wells and integrating fiber optic communication lines and power lines into the body of the pipe.
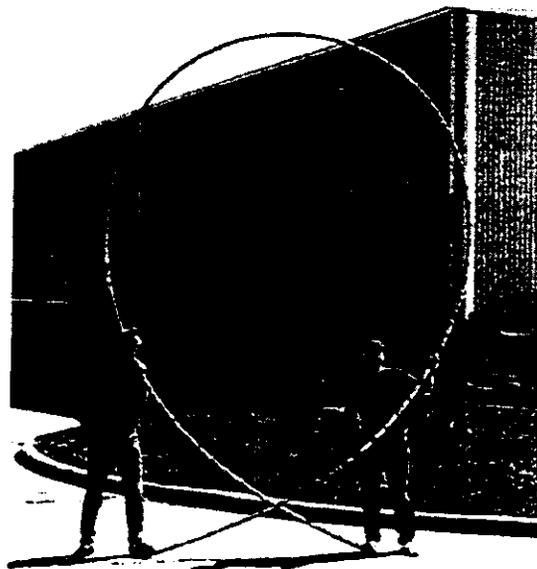
Figure 16.- Spoolable high pressure pipe
illustrating bending capability.

Table IV summarizes some of the expanded applications being considered for spoolable pipe. Spoolable composite pipe is being studied for use in pipe line cleanout both onshore and subsea and for operations in highly deviated or horizontal wells. Spoolable pipe is being explored in Europe for use as completion tubing in coal bed methane wells. Current production of spoolable pipe is for sizes up to 4-inch diameter. If the capability to extend this to the 6-inch to 8-inch range develops, the product could provide a significant advancement as a new concept for compliant risers. Another potential application for large diameter spoolable pipe would be as the return line for riserless drilling. The absence of intermediate joints and rapid spoolable deployment provides high economic and operational incentive. Composite Coiled Tubing is also being explored for use in drilling operations to convey the mud motor downhole and supply the mud and pressure to drive the mudmotor.

TABLE IV.- SPOOLABLE COMPOSITE PIPE POTENTIAL APPLICATIONS.

- Coiled Tubing
- Production Tubing
- Saltwater and CO2 Injection Lines
- Drill Pipe
- Completion Tubing
- Velocity String
- Capillary Tube
- Subsea Lines
- Flexible Risers
- Use in Remote and Environmentally Sensitive Area.
- Arctic Temperature Applications
- Refinery Applications

Hydril is working under a NIST ATP program to develop spoolable tube products and fabricated and installed approximately 3000-ft of 1.5-inch in an onshore flowline application. The tubing was handled using a coiled tubing rig as shown in Figure 17, but the tubing was not run into a live well.

Fiberspar Tubular Products recently introduced a commercial line of spoolable pipe products designed for production tubing, line pipe and coiled tubing applications. The production tubing and line pipe use glass fibers in an epoxy matrix while carbon fibers provide the higher strength and stiffness needed for the more demanding coiled tubing application[27]. Halliburton is a partner in the development with Fiberspar and recently conducted a series of tests in West Texas wells with 7500-ft lengths of 1.5-inch diameter composite coiled tubing. The coiled tubing was run using a coiled tubing rig and work accomplished included clean-out of sand and acidization to stimulate the well. In another effort by Fiberspar, long sections of 2-inch pipe line with a 1600 psi operating pressure was installed as line pipe in west Texas (shown in Figure 18). The line pipe used for water injection was buried in a previously dug trench. Although the pipe costs more than conventional fiberglass pipe, installation costs are lower and elimination of most of the couplings reduces the risk of leaks.
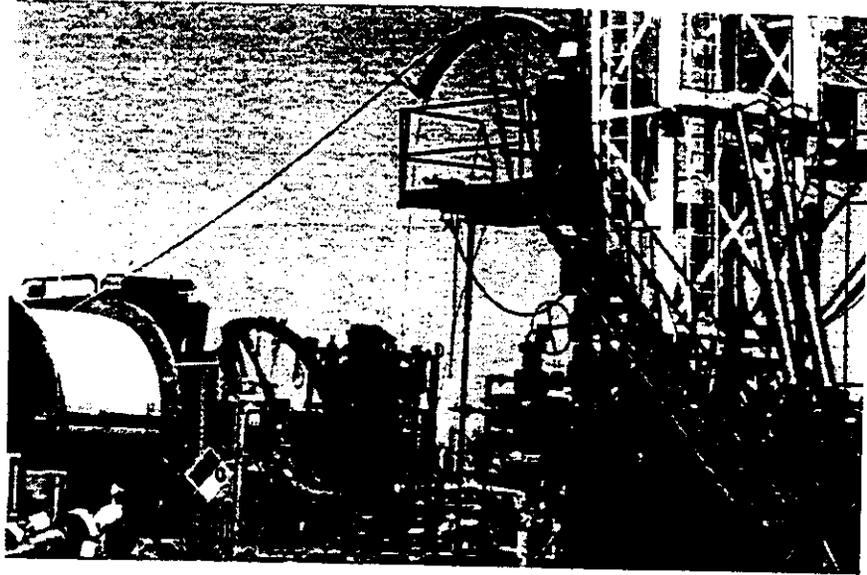
Figure 17.- Spoolable composite pipe deployed using coiled tubing rig. (Hydrill)
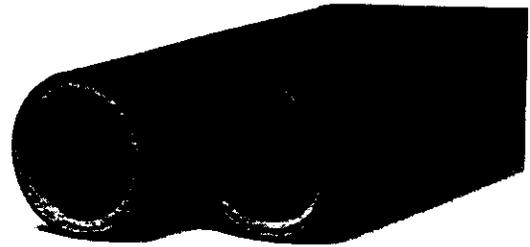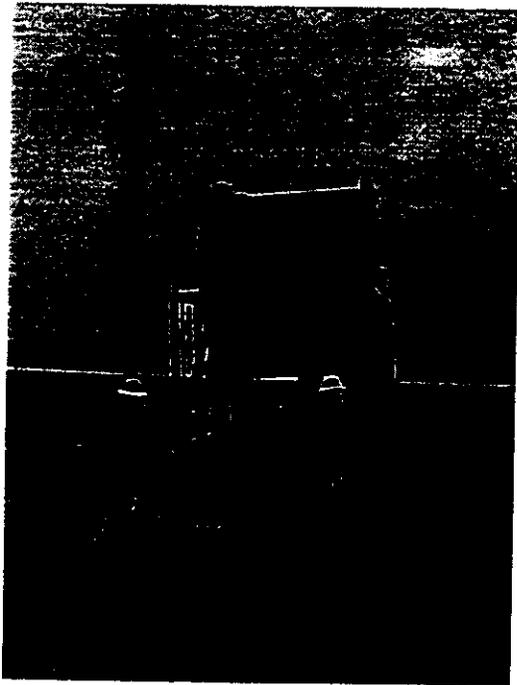
Figure 18.- Deploying 2-inch diam. spoolable composite line pipe. (Fiberspar Spoolable Products and Halliburton)

In another development, Compipe a/s was awarded a contract to supply 16 km of spoolable pipe for the Asgard project for use as subsea methanol injection lines (Figure 19). The pressure rating for the 3-inch diameter spoolable pipe is 5600 psi. The price of the composite pipe with a PEX liner is projected to be about the same cost as carbon steel and less expensive than other alternatives. The lower thermal conductivity of composite pipe also provides an advantage for maintaining the temperature of oil transported subsea which of course, helps prevent hydrate and paraffin formation. Double walled and insulated spoolable composite pipe could also be designed to address the temperature reduction problem.
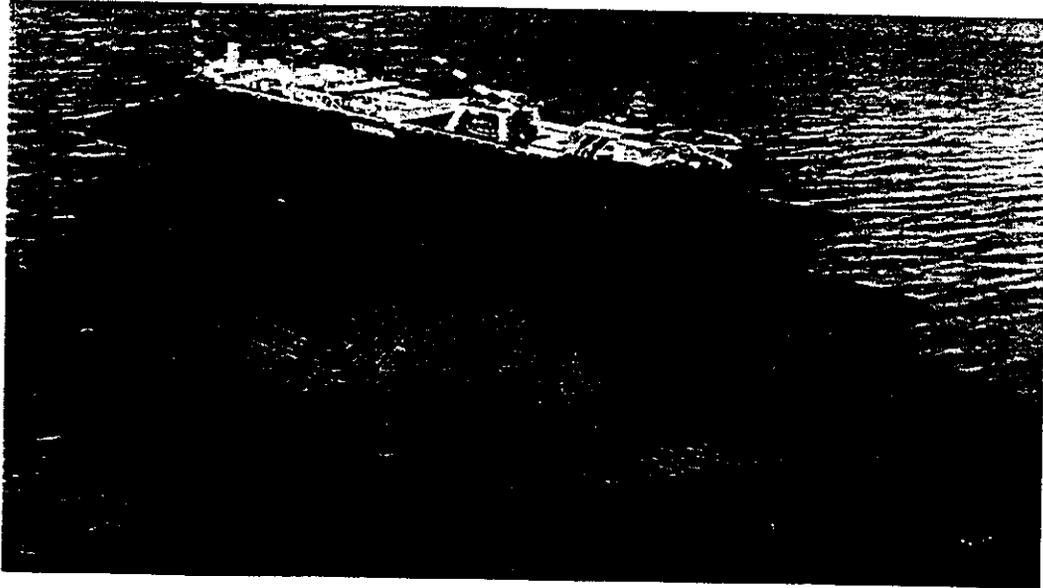
Figure 19.- Illustration of composite spoolable pipe for subsea injection lines, flowlines, and flexible risers. (COMPIPE a/s)

Platform Primary Structure

Several companies have proposed making platform deck structure using composite pultruded elements which can be used individually as beams or assembled into a large integral structure using VRTM or other joining methods. Pultruded structural elements are also being developed for infrastructure bridge construction. A 36-inch beam made by Strongwell is shown exiting the pultrusion machine in Figure 20. The insert on the right shows the beam cross-section geometry. The beam is a hybrid construction with high stiffness carbon placed in the caps and the remainder of the cross-section reinforced with glass fibers. Cells are incorporated in the web to increase the torsional stiffness. Pultruded composite beams are being considered for structural members in platform deck construction.
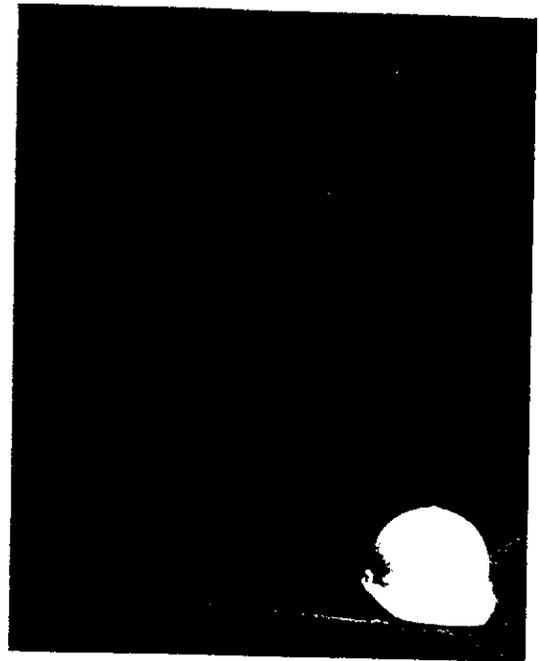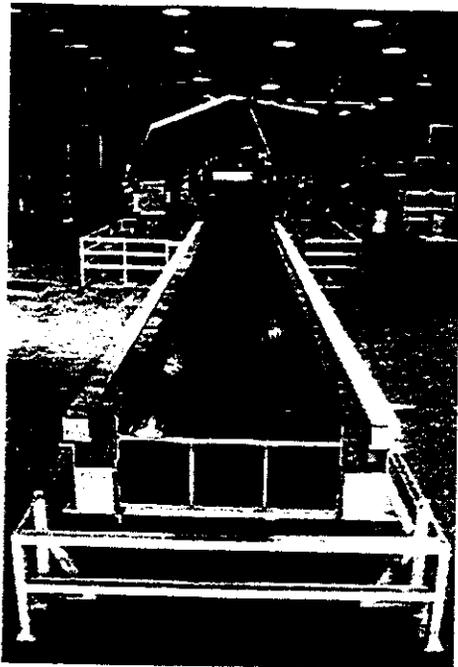
Figure 20.- Large (36-inch deep) pultruded beam with carbon selective reinforcement in the caps and web cells for torsional stiffness. (Strongwell)

Process Equipment / Pressure Vessels

Many of the pressure vessels and process equipment used on offshore platforms could be constructed from composite materials[28]. The riser tensioner accumulator pressure bottles used on recent TLPs installed in Gulf of Mexico shown on Figure 21 were constructed of composite materials[29]. The accumulator bottles have a HDPE thermoplastic liner over which is wound a carbon and S-glass hybrid with an epoxy resin. The bottles have a safety factor of 5 and were designed according to ASME Code Section X. The vessels are certified for 35 years of service with a 3000 psi pressure rating. Even though the pressure vessels are constructed using carbon, the cost is less than steel bottles and in addition provide weight savings of approximately 66 percent.
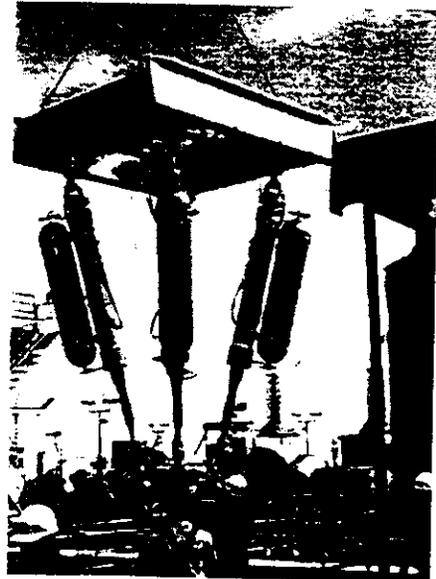
Figure 21.- TLP riser tensioner accumulator bottles made from composite materials .
(Lincoln Composites)

In another program sponsored in Norway, a fiberglass mud gas separator was developed and field tested. The 15-ft diameter vessel was designed for 10.3 bar pressure. The separator was fabricated using ECR glass fibers and vinyl ester resin making it highly resistant to the mud, salts, caustic soda, and corrosive environment experienced in drilling. The mud gas separator was installed on Smedvig Technology's drilling vessel, the West Vanguard in 1995 and used in drilling operations. The vessel saved 50 percent weight compared to a steel vessel.

Accommodation Module

Modern fire resistant materials and technology make it feasible to construct living quarters using composite materials. Offshore Design Engineering (UK) conducted an extensive study to evaluate the merits of using a composite wall in the construction of an offshore accommodation module. The focus of the program was on structural wall panels constructed using phenolic resin reinforced with fiberglass. ODE's basic structural concept was to use a steel frame clad in phenolic panels. The phenolic/glass panels would be attached to a steel portal frame and would serve to insulate the steel from the heat of a fire and to provide shear stiffness to the structure. ODE worked closely with phenolic panel fabricators to develop a manufacturing involving Resin Transfer Molding (RTM). The program included material fire testing in which toxicity, smoke emissions, rate of burn, fire spread and heat transfer were measured. Material mechanical properties were also measured and connectors and joints details studied. Joining is one of the most critical aspects of the ODE concept since joints must maintain their integrity to restrict the passage of smoke during a fire. The program culminated with the construction of a two story, eight room cabin mock-up which was subjected to structural and fire tests. A set of guideline specifications were also developed[30]. Additional effort is needed to address some of the unresolved fire performance issues. A photograph of the two story module under construction is shown in Figure 22.
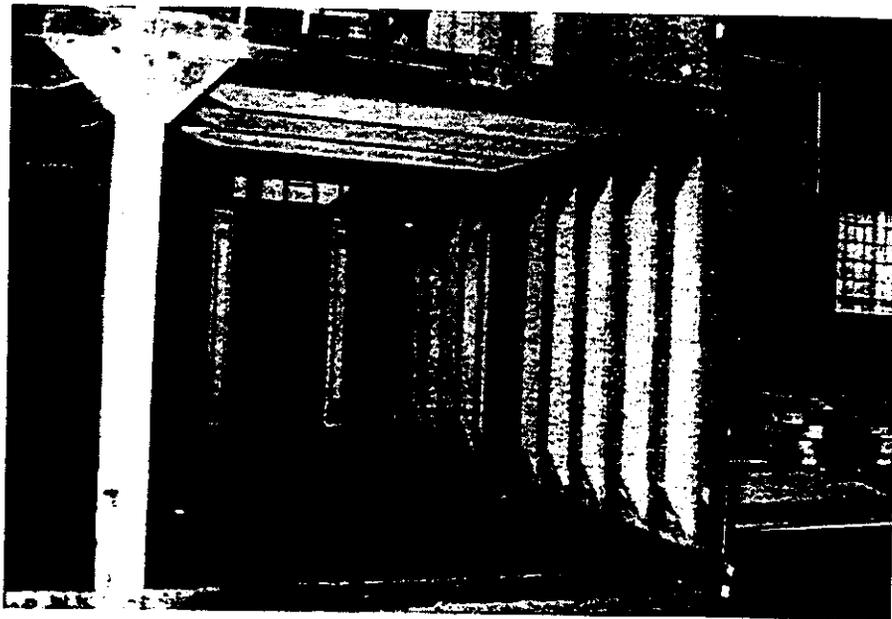
Figure 22.- Glass/Phenolic stiffened panel accommodation experimental module .

TLP Tendons

A light-weight composite tendon could extend the water depth practical for TLPs well beyond currently perceived limits. TLP tendons provide one of the most productive applications for composite materials because the design requirement of predominately axial tension loads best utilizes composite materials high unidirectional strength and stiffness. Several concepts for a composite tether have been proposed including: (1) parallel-lay graphite rope composed of multiple unidirectional graphite/resin rods, (2) Kevlar rope composed of an assembly of strands without resin, and (3) a thick-walled graphite/resin tubular.

British Ropes in the late 1980's explored the design of a composite rope constructed of many strands of small diameter carbon/resin rods[31]. The rods are laid down in the assembly with a small helix and the assembly is encapsulated in a plastic cover which allows the rope to be spooled for transport and deployment. The graphite/resin rods have a small diameter (around 0.2 inch) and would be pultruded in multiple dies for low-cost manufacturing. The rod rope termination involved potting the ends in a potted conical receptacle. A photograph showing the rope being tension loaded is shown in Figure 23.
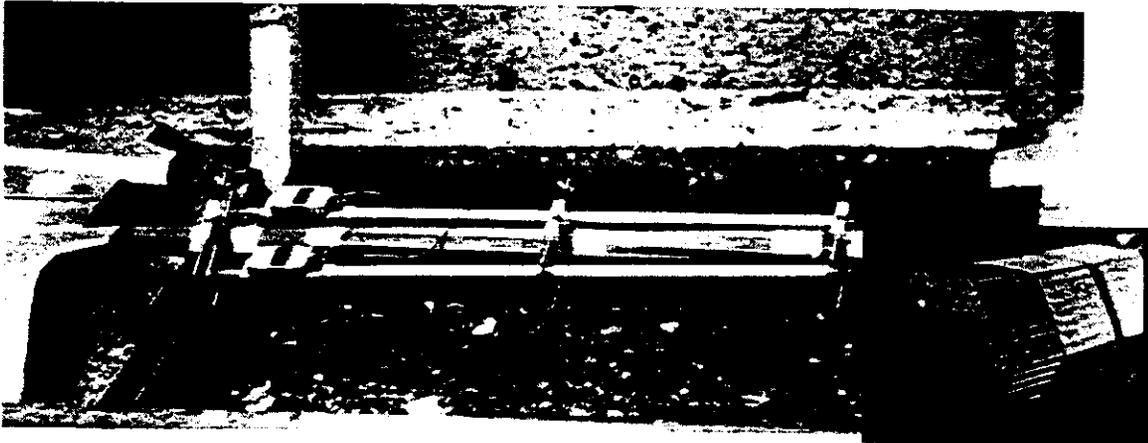
Figure 23.- Tension testing carbon rod rope tendon.

An alternative concept proposed for a tether is a filament-wound, thick-walled composite tube constructed of alternating layers of plus and minus oriented layers. For small winding angles from axial (<10 degrees), the reduction in modulus from unidirectional is small. A ±10° lay-up would reduce the axial stiffness by approximately 8 percent. The filament wound tube could not be spooled but could be assembled in long lengths and towed to location much like the Jolliet and Heidrun TLP steel tube tendons. The tube could also be designed to be neutrally or even positively buoyant,[32] however, the design to resist collapse would make the design inefficient compared to a rod rope concept. A ±10 degree design would have very limited resistance to external pressure while a tube designed to resist collapse would compromise axial stiffness.

Synthetic Fiber Mooring Rope

Synthetic fiber mooring ropes have been successfully deployed by Petrobras[33] in Brazil, but as yet there has been no deployment in United States waters. A sketch illustrating taut leg and catenary configurations along with a TLP tendon are shown in Figure 24. Studies indicate that significant improvements in performance and cost can be achieved using a polyester mooring rope for station keeping on deepwater platforms. Several programs have been initiated in the United States including a field test program by Deepstar and an aborted test program in 1998 by BP and Aker caused by failure of the installation equipment. The merits of the synthetic fiber mooring rope are sufficient to justify supporting further technology development to ensure that the technology is ready and acceptable to operators and government regulators. There is also a need for a more scientific basis for design which better captures the viscoelastic response of synthetic fibers and the geometric nonlinearities of fiber rope response.

Tension
(Carbon Rope,
Kevlar 49 Rope)

Taut
(Polyester Rope,
Kevlar 29 Rope)

Catenary
(Polyester Rope,
Kevlar 29 Rope)

Chain
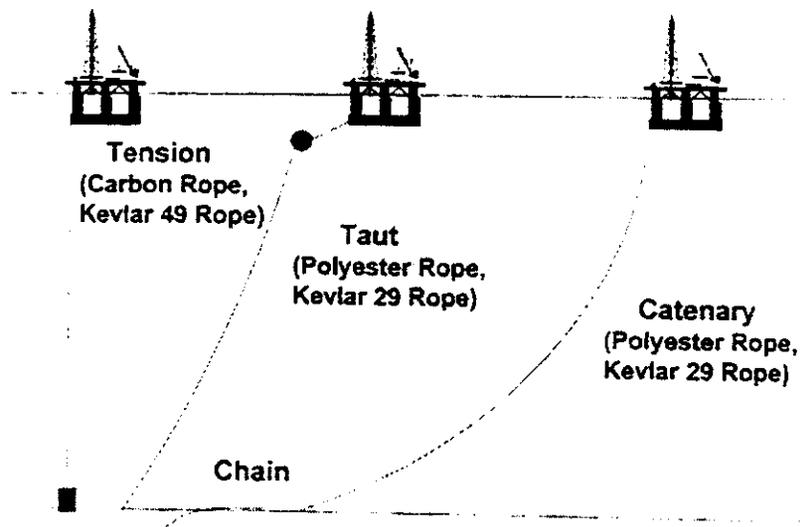
Figure 24.- Synthetic fiber mooring rope and composite tendons.

CONCLUDING REMARKS

Current applications of composites in the offshore oil industry are primarily fiberglass based secondary structures such as low-pressure pipe and gratings. Considerably more research and development is needed to provide the assurance necessary to place primary structures and systems into offshore service. A comprehensive materials and design experience database is also needed. The benefits of saving weight on an offshore floating platform are complex to evaluate and to accurately assess the merit; it is usually necessary to conduct a systems level analysis. To be adopted by industry, composite products must either provide enabling capability or yield significant cost savings on an initial or life cycle basis without imposing increased risk. Deepwater development has created high interest and expectation for composites and both enabling and cost savings have been shown to be possible. The oil industry has traditionally used steel and a bias

toward steel has to be overcome. However, the barrier associated with a reluctance to consider composites is coming down, which allows composite materials to compete based on their merit.

It is important in evaluating the merits of composites that an integrated approach be used to capture the synergistic benefits of weight savings and lower maintenance on other components and systems on the platform. Successful introduction of new products also requires that the interests of all the participants with invested interests be considered including the materials supplier, composites manufacturer, system designers, oil company project decision makers, and the regulatory agencies. The availability of industry endorsed standards and guidelines are particularly important to the process of receiving regulatory agency approval. During the last decade, considerable progress has been made in this area with most of the effort focused on FRP piping and secondary structure applications such as gratings. As advanced composite structure concepts are introduced such as risers, pressure vessels, coiled tubing, drill pipe, subsea flow lines, etc.; recommended practice documents will be required to specifically address these new applications.

One of the effects of new technology advancements is to challenge the existing infrastructure and technology. One of the effects composite materials had for the aircraft industry was to challenge aluminum manufacturers who responded by developing improved aluminum alloys. We see some of this challenge now being met by the manufacturers of steel and steel products. For the designer, there are many more material choices including steel alloys as well as titanium and composites. In this environment, competing technologies lead to better solutions tempered by competitive market pressures.

REFERENCES

1. Williams, Jerry G.: "Offshore Experience - Opportunities For Composites In The Offshore Oil Industry". *The Use of Composite Materials In Load Bearing Marine Structures.* National Conference convened by the National Research Council's Marine Board. Washington, D.C. September 25-26, 1990.

2. Vennett, Richard M.; Williams, Jerry G.; Lo, K. Him; and Ganguly, Partha: "Economic Benefits of Using Composites for Offshore Development and Operations". *Composite Materials for Offshore Operations – 2,* S. S. Wang, J. G. Williams, and K. H. Lo, Eds., American Bureau of Shipping, 1999, pp. 3-16.

3. Williams, Jerry G.: Developments in Composite Structures for the Offshore Oil Industry. Offshore Technology Conference Paper 6579, Houston, TX, May 6-9, 1991.

4. Salama, Mamdouh; Borleske, Steve; and Williams, Jerry G.: "Composites for Marine Construction". *International Workshop On Advanced Materials For Marine Construction,* Glen R. Edwards, William Hanzalek, Stephen Liu, David L. Oslson and Charles Smith, Eds., American Bureau of Shipping, 1997, pp. 311-330.

5. Botros, Fikry; Williams, Jerry; and Coyle, Edward: Application of Composite Materials In Deep Water Offshore Platforms. Offshore Technology Conference Paper 8500, Houston, TX, May1997.

6. Salama, M. M.: Some Challenges and Innovations for Deep water developments. Offshore Technology Conference Paper 8455, Houston, TX, May 1997.

7. Stone, Robert H.: "Dissimilar Materials Separation". *Engineered Materials Handbook, Volume 1, Composites*. ASM International, Metals Park, Ohio. pp. 716-718

8. Ciraldi, S. W.: Fiberglass Firewater Systems For Offshore Platforms. Offshore Technology Conference Paper 6926, Houston, TX, May 4-7, 1992.

9. OLF Recommended Guidelines On Specification For Composite Piping Offshore. Oljeindustriens Landsforening sponsored specification prepared by Advanced Materials A/S. November 1991.

10. Specifications and Recommended Practice For The Use Of GRP Piping Offshore. UKOOA. March 1994.

11. Williams, J.G.; and Silverman S.A.: Composites Technology Used Offshore With Synergy to Offshore Applications. Offshore Technology Conference Paper 11062, Houston, TX, May 3-6, 1999.

12. Houghton, C. J.: "Composites Use On Platform Topsides: A Recent Case History and Future Prospects". *Composite Materials for Offshore Operations – 2*, S. S. Wang, J. G. Williams, and K. H. Lo, Eds., American Bureau of Shipping, 1999, pp. 17-31.

13. Ordu, P. and Guichard: "Design and Tests of High Performance Composite Tubes for Use in Deep water Drilling and Production Systems". *OMAE Specialty Symposium on Offshore and Arctic Frontiers*, M. M. Salama, ed., ASME, 1986, pp. 353-359.

14. Sparks, C., Odru, P., Bono, H., and Metivaud, G.: Mechanical Testing of High Performance Composite Tubes for TLP Production Risers. Offshore Technology Conference Paper 5797, Houston, TX, May, 1988.

15. Sparks, C. P.; and Schmitt J.: Optimized Composite Tubes for Riser Application. Proceedings of the Ninth International Conference On Offshore Mechanics and Arctic Engineering. Houston, TX. Volume III - Part A. Feb. 18-23, 1990. pp. 1-8.

16. Baldwin, Donald; Newhouse, Norman; and Lo, K. Him.: "Composite Production Riser Development". *Composite Materials for Offshore Operations – 2*, S. S. Wang, J. G. Williams, and K. H. Lo, Eds., American Bureau of Shipping, 1999, pp. 115-128.

17. Johnson, Douglas B.; Baldwin, Donald D.; and Long, Randy J.: Mechanical Performance of Composite Production Risers. Offshore Technology Conference Paper 11008, Houston, TX, May 3-6, 1999.

18. Galle, Gary L. and Whitehead, Justin M.: Development of Oilfield Composite Systems – Test-Verified Design Solutions. Offshore Technology Conference Paper 11007, May 3-6, 1999.

19. Salama, Mamdouh M.; Murali, Jagannathan; Baldwin, Donald D.; Jahnsen, Ove; and Meland, Thor: Design Considerations for Composite Drilling Riser. Offshore Technology Conference Paper 11006, Houston, TX, May 3-6, 1999.

20. Sas-Jaworsky, Alexander; and Williams, Jerry G.: Development of Composite Coiled Tubing for Oilfield Services. Society of Petroleum Engineers 68th Annual Technical Conference and Exhibition, SPE paper 26536, October 1993.

21. Quigley, P. A.; Nolet, S. C.; Williams, J. G.; and Sas-Jaworsky, A.: Development and Application of a Novel Coiled Tubing String for Concentric Workover Services. Offshore Technology Conference Paper 8456, Houston, TX, May 1997.

22. Quigley, Peter; Fowler, Hampton; Nolet, Stephen; and Berning. Scott: "Update On Composite Coiled Tubing Developments and Horizontal Well Applications". *Composite Materials for Offshore Operations – 2*, S. S. Wang, J. G. Williams, and K. H. Lo, Eds., American Bureau of Shipping, 1999, pp. 303-318.

23. Asdal, Bent; and Hansen, Allan Boye: Composite Spoolable Flow Lines. *Composite Materials for Offshore Operations – 2*, S. S. Wang, J. G. Williams, and K. H. Lo, Eds., American Bureau of Shipping, 1999, pp. 319-328.

24. Walsh, Thomas J.; Peterman, Charlie P.; Reynolds Harris A.; and Lundberg Chris A.: "Advances in Manufacturing Technology for Continuous Composite Tubing". *Composite Materials for Offshore Operations – 2*, S. S. Wang, J. G. Williams, and K. H. Lo, Eds., American Bureau of Shipping, 1999, pp. 289-301.

25. Wolfe, Donald; and Baron, John: Unbonded, Multiple-Layer, Flexible Composite Pipe. *Composite Materials for Offshore Operations – 2*, S. S. Wang, J. G. Williams, and K. H. Lo, Eds., American Bureau of Shipping, 1999, pp. 329-340.

26. Frost, Simon R.: "The Development of Re-Inforced Thermoplastic Pipes for Use in the Oil Industry". *Composite Materials for Offshore Operations – 2*, S. S. Wang, J. G. Williams, and K. H. Lo, Eds., American Bureau of Shipping, 1999, pp. 341-359.

27. Koshak, W. E.; et. al.: A Summary of Recent Successes and Challenges in the Development of Spoolable Composite Tubulars. SPE Paper 54506. SPE/ICoTA Coiled Tubing Roundtable, Houston, May 1999.

28. Anisdahl, Lars; Wang, Dag T.; and Stokke, Reidar: Study of the Design & Use of GRP Tanks and Vessels Offshore. *Composite Materials for Offshore Operations – 2*, S. S. Wang, J. G. Williams, and K. H. Lo, Eds., American Bureau of Shipping, 1999, pp. 261-274.

29. Baldwin, Donald; Newhouse, Norman; and Lo, K. Him: High Pressure Composite Accumulator Bottles. *Composite Materials for Offshore Operations – 2*, S. S. Wang, J. G. Williams, and K. H. Lo, Eds., American Bureau of Shipping, 1999, pp. 275-286.

30. Guidelines for the Application of Fiber Reinforced Plastic Materials To Topsides and & Superstructures In A Marine Environment. JIP Report by Offshore Design Engineering and British Maritime Technology. 1992.

31. Walton, J. J. and Yeung, Y. C.: Flexible Tension Members from Composite Material. Proceedings 6th International OMAE Symposium, (M. M. Salama, et. al, eds.) ASME, V. 3, pp.7-14. 1987.

32. Hanna, Shaddy Y.; Thomason, William H.; and Williams, Jerry G.: Influence of Tension, Weight, and Hydrostatic Pressure On TLP Tendons. Journal of Waterway, Port, Coastal, and Ocean Engineering, Vol. 115, No. 2, March 1989.

33. Del Vecchio, C.J.M. and Costa, L.C.S.: Station Keeping In Deep And Ultradeep Waters. Offshore Technology Conference Paper 10778, Houston, TX, May 1999.

Economic Considerations in Material Selection
for Offshore Oil & Gas Production Applications
D. Pattle, Wyman-Gordon Co.

Economic Considerations in Material Selection for Offshore Oil & Gas Production Applications

Derek Pattle

Vice President Energy Products

Wyman-Gordon Co.

WYMAN GORDON

Carbon Steel

- Process Pipe - Line Pipe Applications
- Initially Carbon Steel - X52
- Easily Welded & Fabricated
- Problems with corrosive environments
- Cost less than $1000/tonne
- Reference "Base Price".

410 SS Material – 12 Cr

- Progression onto 410 SS material
- Advantage resistant to Sulphide corrosion
- Difficult to weld – pre-heat & stress relieve
- Problem with "sweet" CO_2 corrosion.
- Cost of 410 SS – 2 to 3 times Base Price.

WYMAN GORDON

Duplex Steel - 22 Cr

- Next progression - mainly North Sea driven

- Use of Duplex - 22 Cr material

- Higher strength - resistant to CO_2 corrosion

- Not resistant to H_2S

- Initially difficult to weld and fabricate

- No pre-heat or stress relief requirement

- Cost about 5 to 6 times Base Price.

WYMAN GORDON

Super-Duplex - 25 Cr

- Use of 25 Cr or Superduplex increased

- Improved corrosion - both CO2 & H2S

- 20% improvement in both yield & UTS

- More difficult to weld than duplex

- Cost approximately 7 to 8 times the Base Price.

WYMAN GORDON

6 Moly Material

- Material mainly used in the Sea-Water applications

- Has excellent corrosive resistance - especially at very low temperatures

- Niche use in gas processing pipe-work - for blow-down conditions

- Cost about 8 to 9 times the Base cost.

WYMAN GORDON

Sea Water Systems

- Progression of materials
  - Carbon – Cu Ni – 6 Moly – 25 Cr
- Standardise on one alloy 25 Cr for the whole platform – but.......
- Cp Ti used – reputation for high cost
- Troll & Hibernia Ti offers 30 to 50 year life

WYMAN GORDON

Ni Based Alloys

- Only used in the very corrosive applications
- Quatar, India and proposed for Indonesia
- 825 requires some cold working for the strength; 925 is age hardening - 625 high Ni & Cr
- Very difficult to weld and fabricate
- Cost between 15 to 20 times Base cost.

WYMAN GORDON

Clad Pipe 1

- Offers the benefits of high corrosion resistance, strength of steel and at a lower cost.

- Various techniques – mechanical; weld; metallurgical bond.

- Mechanical OK for straight pipe – but limited elsewhere

WYMAN GORDON

Clad Pipe 2

- Recent development in the co-extrusion of clad pipe LIDB & Seamet processes.

- Excellent bonding - capable of fittings, bending and reeling.

- Reasonably straight forward welding and fabrication

- Cost about 5 to 6 times Base cost - with opportunities to reduce.

WYMAN GORDON

Ti Alloys 1

- Cp Ti for sea-water - but either grade 23 or 29 for riser applications

- Why Ti - when costs can be up to 100 times base cost

- Double strength & two thirds density

- 3 lb steel for every 1 lb of titanium

- Excellent low cycle fatigue properties

Ti Alloys 2

- High pressure, high temperature capability
- Lower overall weight – deep-water this is critical
- Improvements in processing improving yield
- Costs on an equal basis could be as low as 15 times base costs – and maybe the only technically acceptable solution.

13 Cr Material

- High strength & corrosive resistant material

- Welding almost impossible

- Super 13 Cr developed – (Ni & low C) – has overcome some of the problems

- Asgard & NAM on-shore pipe-lines use Super Cr to replace Duplex

- Cost up to 4 times Base cost.

High Strength Steels

- 85 to 110 ksi Steels - offer lower weight - but no corrosion

- Impossible to weld (to meet NACE stds)

- Weldless connectors together with a double ended upset pipe - offers a solution, that can significantly reduce weight and costs.

WYMAN GORDON

THOR & Double Plus Products
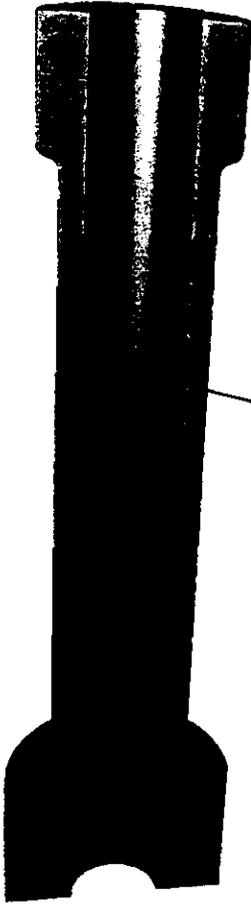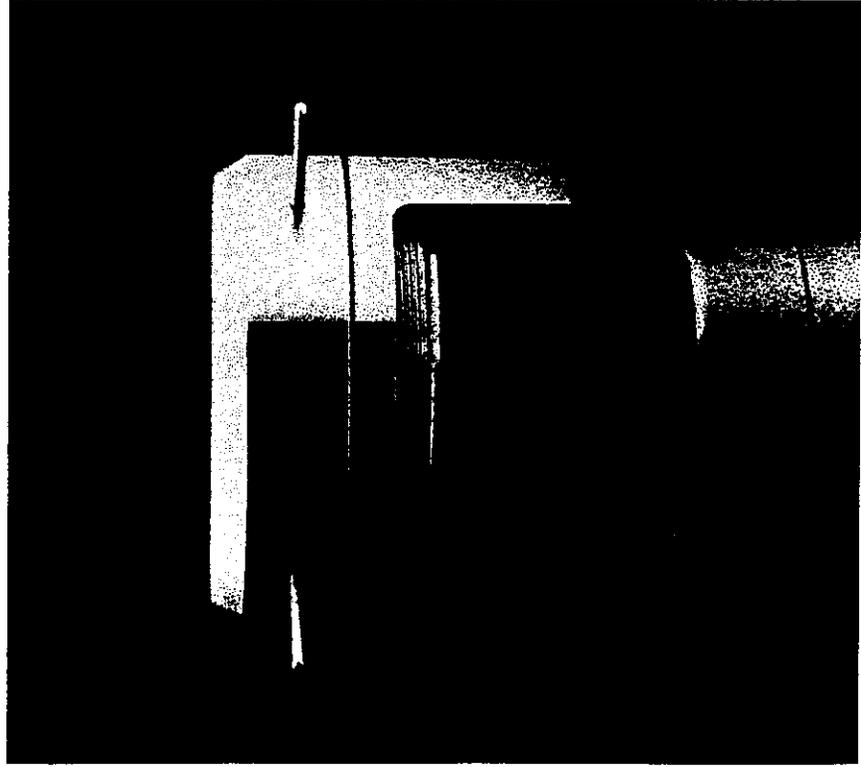
Double Plus

THOR

WYMAN GORDON

Theme Papers

Overview on Materials Challenges

J.F. Jenkins, Nickel Development Institute

Metallic Coatings for Corrosion Control of Marine Structures

D.T. Peters and H.T. Michels, Copper Development Association Inc.

C.A. Powell, Nickel Development Institute

Coatings: Organic

R.D. Granata, SeaTech - Florida Atlantic University

Cathodic Protection of Offshore Structures and Pipelines –Historical Development, Present Knowledge, and Future Challenges

W.H. Hartt, Center for Marine Materials - Florida Atlantic University

High Strength Fasteners for Seawater Immersion Service

D.M. Aylor, C.A. Bowles, R.L. Tregoning, and M.A. Gaudett

Naval Surface Warfare Center, Carderock Division

Structural Testing of Corroded Offshore Tubular Members

J.M. Ricles, M. Hebor, and D. Paterson, Lehigh University

Corrosion and Materials Challenges for Deep Water Oil and Gas Production

R.D. Kane, M.S. Cayard, and H.R. Hanson, InterCorr International, Inc.

Corrosion Protection of Ballast and Cargo Tanks of Crude Oil Tankers

R.T. Huang, Chevron Shipping Company

THEME PAPER

OVERVIEW ON MATERIALS CHALLENGES

by

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Nickel Development Institute
Toronto, Ontario, Canada

Introduction

There are many challenges facing the producers and users of materials in the year 2000 and beyond. While there certainly will be many new materials developed in the future, the primary challenge is to insure that the optimum material is used for each application. Selection of materials is most effective when it is an integral part of the design process. Optimization of materials is usually conceived to be the use of a material that will give the lowest life-cycle cost. This is only true if the life cycle cost of the entire system is considered and the cost factors do not vary with time. Due to fluctuations in many of the cost factors with time, the optimum material for a specific application today might not be the optimum material for the same application at a later date.

Many groups have a role to play in the optimization of materials applications. The materials industry develops new materials and characterizes their properties. The materials industry must also inform the user regarding potential applications for these newly developed materials as well as for more traditional materials. The materials industry may also assist the user in the selection and use of specific materials. Other groups such as professional societies and standards organizations also have a role in the materials selection and optimization process. The selection of the optimum material for specific applications is, and will continue to be the primary materials challenge for the year 2000 and beyond.

Salient Material Characteristics

There are many material characteristics that are potentially important in the selection of a material for a specific application. No single material is ideal for all applications. If there were an ideal material for all applications, there would only be a market for one material. In the matching of a material to an application some of the following factors can be important:

> Strength
> Ductility
> Toughness
> Weight
> Corrosion Resistance
> Biofouling Resistance
> Elastic Modulus
> Physical and Electrical Properties
> Cost
> Fabricability
> Availability

Strength is an important factor in the selection of materials for most applications. However, strength alone is seldom the only factor in the selection of a material. In fact, while applied stress must not exceed the strength of the material, more structures are designed for a specific stiffness or resistance to buckling than are designed simply to resist uniaxial tension.

To properly utilize published or measured values of materials characteristics, it is important that the designer know how these values are derived so that the values can be properly interpreted and applied. A simple example of this is given below for a commonly used materials characteristic; yield strength.

Two values of strength are commonly reported, yield strength and ultimate tensile strength. The value most pertinent to most designs is the yield strength. The concept of yield strength was derived from the unique property of soft carbon steel. Soft carbon steel can be loaded to specific value with fully elastic response (strain proportional to stress). If loaded above this yield stress, its behavior becomes inelastic and it will plastically deform. This is shown in Figure 1.
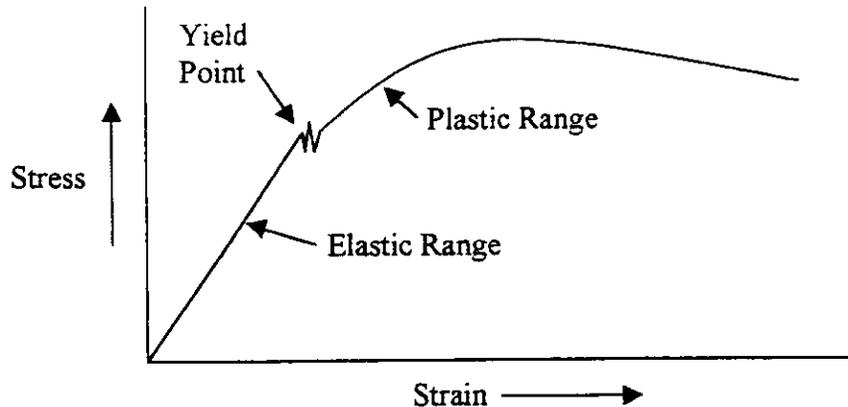
Figure 1. Yield point in loading of carbon steel.

Although a yield strength is reported for other metals and alloys, many do not exhibit a true yield point as in the case of soft carbon steel. As shown in Figure 2, they begin to depart from truly elastic behavior at very low applied stress. For these materials, the stress required to give an arbitrary amount of plastic deformation, commonly 0.2%, is reported as the yield strength.
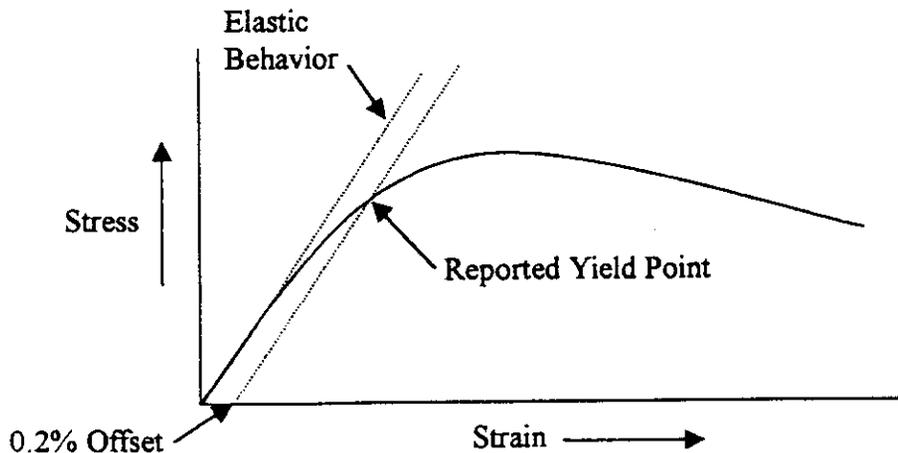
Figure 2. Arbitrary yield point for an aluminum alloy.

This inelastic behavior below the reported yield point stress can be an important factor, particularly when the structural element will be subjected to repeated loading at a stress that is an appreciable percentage of the yield strength. At each application of the load, the material will deform plastically and not return to its original size. This effect is a major factor in the design of structures for fatigue loading applications and can also be important when plastic deformation will affect fit or alignment of parts. Thus, understanding how material property values are derived is important in their application to design.

Ductility is a measurement of the amount of deformation that a material can withstand without rupture. As in the case of strength, the ductility of many metals and alloys is dependent on the test conditions and is difficult to apply directly to design. However, high levels of ductility are desirable in most applications. In general, within groups of similar alloys, strength and ductility are inversely related. Higher strength alloys usually have lower ductility. Thus materials with appropriate strength, but not higher strength than is actually required, usually give the optimum performance. Many more failures occur to brittle fracture because the material was insufficiently ductile than occur because the material had insufficient strength and failed ductility due to overload. Selection of metals for a balance of strength and ductility is often a negotiation between the designer who wants to use a high strength material to give a reserve of strength and a metallurgist who wants to use a more ductile material with just enough strength to avoid ductile failure.

Ductility is poorly defined for many composite materials both in terms of measuring the ductility of the material in a meaningful way, and in determining the required ductility for a specific application. This will certainly improve as there is more development and experience in the use of composite materials.

Toughness is the ability of a material to absorb energy without rupture. Energy is a function of both force (applied load) and distance (strain) and is closely related to the area under the stress strain curves shown in Figures 1 and 2. A very ductile material with the same strength as a less ductile material will have a higher toughness. Many materials are notch sensitive and show greatly reduced toughness when a flaw or other feature that causes localized stress concentrations is present. One example of this is the brittle fracture of steel at a pre-existing crack or flaw. The toughness of many materials is temperature sensitive. Such materials are said to have a "ductile – brittle" transition temperature. Carbon and alloy steels are examples of materials having a ductile – brittle transition temperature. The toughness of other materials such as aluminum and some stainless steels is relatively insensitive to temperature. As most structures have some level of stress concentration, toughness is an important factor in design. Toughness is also frequently used to define critical flaw sizes, and thus the required sensitivity of non-destructive testing techniques for critical equipment such as pressure vessels.

Weight is an important material property in many applications. The use of lightweight materials results in reduced dead weight loads, which can reduce the stress on supporting materials resulting in even lighter structures, and reduction in the amount and cost of material required. Strength to weight ratio (expressed here as yield strength (MPa) divided by the specific gravity of the alloy) is frequently used as selection criteria for materials. Materials have a very large

4

range of these strength-to-weight ratios ranging from (for metals) from under 25 to over 250. Some composite materials have strength-to-weight ratios exceeding 250.

Corrosion resistance is an important material characteristic in many marine applications. In some cases, the material must be resistant to two or more environments. For example, a piece of oil production equipment may need to be resistant to the produced fluids on the inside as well as to the marine environment on the outside. Other equipment such as heat exchangers are commonly subjected to more than one potentially corrosive environment.

The marine environment is very complex and aggressive towards many materials, both metallic and non-metallic. The corrosivity of the marine environment is primarily due to the presence of large amounts of dissolved aggressive species such as chloride and sulfate. However, many other factors such as temperature and the amounts of dissolved gases such as oxygen and carbon dioxide are variable and have a significant effect on the corrosivity of the environment. These factors are difficult to reproduce in the laboratory and testing in actual operating environments is usually required to adequately characterize materials with regards to their resistance to that environment. Many operating factors such as temperature and flow velocity also affect the performance of materials in marine applications and must be addressed when selecting materials. Many materials require protection from corrosion in marine environments to give satisfactory performance. This protection may be through the application of protective coatings or through other means such as cathodic protection. These protective measures may be effective but the cost of these protective measures must be considered in the economic evaluation of a specific system. It may be more economical to select a material that is initially more expensive but does not require protection or maintenance.

Biofouling resistance is an important factor in many marine applications. Marine organisms will attach to and grow on most materials when exposed to seawater. These organisms can have many undesirable effects such as increasing hydrodynamic drag on ships, increasing the weight of oil platforms and the clogging of pipes and tubes. A few materials such as copper and copper-nickel alloys have inherent resistance to the attachment and growth of these organisms. Other materials may be adversely affected by the attachment of organisms such as barnacles that create crevices on the metal surface. Organic materials may be directly attacked by boring organisms that tunnel into the material for protection, or in the case of wood, may be actually consumed by the organisms.

The attachment of organisms is commonly inhibited by the use of protective coatings or by the injection of biocides into process streams. While effective, these measures are greatly affected by environmental regulations that are becoming more restrictive. The use of inherently resistant materials such as the copper-nickel alloys may become more advantageous as the use of alternative biofouling control measures becomes more restricted.

Elastic modulus is an important factor in most designs. Elastic modulus is the ratio of deformation to applied stress. Materials with low elastic modulus will deform more than materials with high modulus under the same conditions of shape and applied load. The elastic modulus of common materials range from about 70 GPa for aluminum alloys to about 210 GPa

5

for most steels, stainless steels and nickel alloys. Titanium has an intermediate modulus of about 120 GPa.

Physical and electrical properties such as hardness, thermal conductivity, coefficient of thermal expansion, abrasion resistance, magnetic properties and electrical resistivity may be important is some applications and materials with appropriate properties must be selected.

Cost is a very important factor in the selection of any material. As will be discussed below, a common error is to compare costs of materials on a cost per pound basis. As the costs of fabrication and assembly frequently exceed the raw material costs, installed cost is a more pertinent measure of the relative costs of different material. Evaluation of the life-cycle cost of the entire system with different material alternatives is the best way of comparing materials.

Fabricability is different for different alloys. Most alloys must be shaped and joined to make an end-use component. Most alloys are weldable, but with different welding techniques required for each. The cost of fabrication is a very important factor in the installed cost of a component and must be considered in any economic evaluation. In addition to the initial fabrication, repair is an important factor in determining life-cycle costs and materials that are easily repaired in the field may have a long-term advantage over materials that are more difficult to field repair.

Availability of the material in the sizes, shapes and amounts required is another important factor that can be of great practical importance. Many materials such as carbon steel are available in a wide variety of sizes and shapes and in essentially unlimited quantities. Other materials may have more limited availability, primarily due to lack of demand. Most materials are readily available as sheet and plate, but their availability in structural shapes and tubing may be limited. There is no inherent reason for this limited availability in most cases and, if sufficient quantity is required, the material can be fabricated into the required shape. In some cases, due to limited production capacity, the lead times for some materials may be long and this must be considered when selecting materials.

Matching Materials Performance to Design

A designer is confronted with a very large number of variables in the initial stages of design. However, as the design progresses, many parameters become more restricted. For example, some value of strength is usually assumed in a structural design. The use of a material with lower, or higher, strength than assumed in order to meet some other requirement such as corrosion resistance or weight may require a change in the design.

Design as an Iterative Process

Design is seldom a linear process. A design usually involves a series of "what if" considerations and frequently involves backtracking when unforeseen considerations are encountered.
The design process can be visualized as a spiral as shown in Figure 3. In this spiral, the spokes are the design considerations and the spiral is the design process. At each iteration, the variation in each consideration becomes more limited and, in the final design, is fixed.
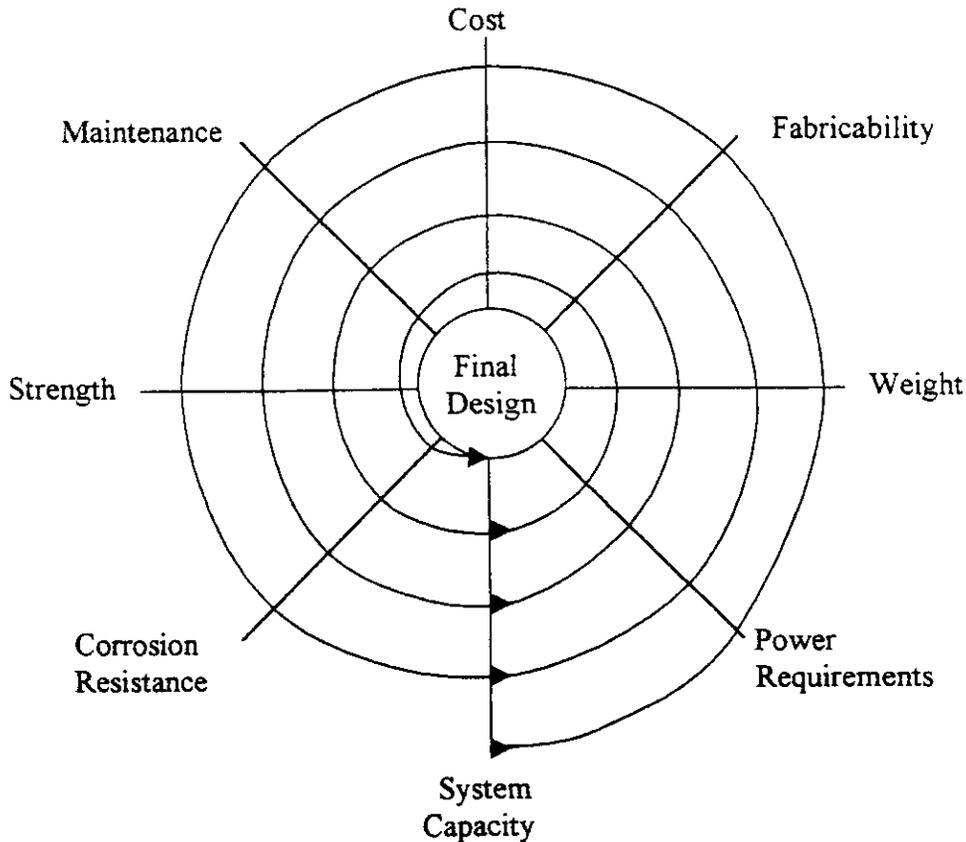
Figure 3. The design spiral.

Establishing of material requirements is an important aspect of the design process. If materials are considered during the design process, reasonable material requirements will be established. If, however, the design proceeds without regards to materials, incompatible materials requirements may be established and the design may need to be significantly adjusted to fit available materials.

The designer usually has significant experience in the design of similar structures and equipment and this experience guides the designer toward the establishment of reasonable materials requirements. If, for example, the stress in a section is over 2,000 MPa, the designer is likely to look carefully at the application to see if the section thickness or some other variable can be adjusted to reduce the stress level to that of a commonly available material. This experience is usually based on two types of experience, knowledge of systems that have failed and knowledge of systems that have been successful.

Experience from systems that have failed is usually based on an analysis of the failure. Failure analysis is routinely performed whenever a serious failure occurs and is relatively straightforward. The site of the initial point of failure is located and the mechanism of the failure is determined. Then the material, operational and environmental factors that allowed the failure mechanism to be active are established. In some cases, there are separate mechanisms for the

7

initiation and propagation of the failure and these are evaluated separately. The results of these failure analyses are commonly published and are frequently used as the basis for the revision of design codes and guidelines. The designer avoids creating conditions that will result in similar combinations of materials, operation and environment.

The repetition of successful experience is somewhat more complicated, but can be very useful in design. Unlike failure analysis, there is no point of failure on which to focus. The entire system, the materials used, the operating conditions and the environment over the life of the system must be considered. Subtle interactions between system components are frequently responsible for system success. For example, the corrosion resistance of many copper alloys in seawater is enhanced by the presence of dissolved ferrous ion. When corroding steel inlet piping was present, the alloys performed well. This was only realized when the steel inlet piping was coated, reducing the ferrous ion levels and allowing increased corrosion of the copper alloys. This effect is now well recognized and is countered by the introduction of ferrous ion into the systems as a corrosion inhibitor.

While failure analyses are commonly performed, success analyses are seldom performed on a formal basis and are less commonly published. Where success has been based on following standard design codes and design, or on a formalized success analysis, repetition of the success in a new design is likely. Where success has been less firmly based it will be more difficult to utilize as a basis for design.

Materials Information Resources

For the selection of an optimum material, the designer must know the properties of a wide range of materials. With increased use of computerized databases, this information is now much more readily available than in the past. Some attempts at expert systems for the selection have been made with varying levels of success. For example, ASM International has developed the MetalSelector software package that considers many materials properties and will select candidate alloys that meet specific materials requirements. These systems however, seldom allow consider all of the pertinent material characteristics such as cost and availability. Additional material property information is usually required to optimize material selection.

The materials industry provides information on a wide variety of materials. In many cases, this information is generic and many producers can supply essentially identical materials. There are also many proprietary materials and information on the properties of these materials is often only available from the suppliers of each proprietary material. Many of these proprietary materials also meet one or more non-proprietary specifications. In many cases, materials are produced to meet specific applications. There are many possibilities for tailoring a given material to a specific application. Alloy composition can be varied within the compositional limits for the alloy to give the desired properties. In addition, thermomechanical treatment of the material can often be varied to produce a material with required properties.

There are many materials specifications developed by standards organizations such as the American Society for Testing and Materials (ASTM), the American Petroleum Institute (API), and Bureau Veritas SA (BVSA). These normally combine requirements for chemical

8

composition and selected mechanical properties such as tensile strength, yield strength and ductility. In most cases, these specifications do not include properties such as toughness, physical properties such as thermal and electrical properties, nor do they specify corrosion resistance. Thus, when selecting alloys based on information in these specifications, much additional information is usually required.

Design codes such those developed by API, ASME and BVSA are usually based on materials conforming to specifications based on alloy composition and strength. In most cases, other properties are not explicitly considered. However, as these design codes have usually been developed based upon experience (both successful and unsuccessful) many of these other assumed properties are actually taken into account even though they are not explicitly specified. This is usually satisfactory as long the new design application and materials are similar to the experience base application but may not be satisfactory if the experience base and the new application differ significantly. For example, a design code based on experience with systems operated in temperate environments may not consider all of the material characteristics required for arctic service.

Optimization of Materials Selection

The optimization of materials selection is frequently performed by evaluating the costs of all of the materials that have the required properties for a specific application. This is best performed as an integral part of the design process but may be performed after the design is essentially complete. Post-design optimization is frequently called value engineering. However, it cannot be overemphasized that, in order to be effective, post-design optimization must consider all life-cycle costs of the system and not simply minimize the initial cost of a part or subsystem.

There are many means of assessing the actual life-cycle costs of a system. Economic analysis methods such as discounted cash flow or return on investment allow for the consideration of the time-value of money and taxes. Each large company usually has its own preferred method for this type of cost analysis and most of these methods give reasonable results as long as realistic cost figures are used as input. It is important to realize that these costs change with time and that the most cost-effective material for an application today may not be the most cost-effective material in future applications Likewise, the most cost-effective material for past applications may not be the most cost-effective material for current applications. Many factors such as the cost of raw materials and the cost of labor for construction and maintenance change appreciably with time and have a very significant effect on the optimization of materials selection.

For the initial cost of a component it is important to use the actual installed cost of the component when evaluating options. This includes, but is not limited to materials, component fabrication, subsystem assembly, packing and preservation, transportation to the worksite, on-site assembly, application of protective coatings, testing and inspection.

In many cases, the selection of materials for one portion of a system affects other parts of the system and their cost. Reduction of component weight has an obvious effect of reducing loads on the support system. Another example is the need for chlorination of seawater when materials that are not inherently biofouling resistant are used for piping and heat exchangers. The cost of

the equipment for chlorination and its operation must be considered if non-biofouling resistant materials are used. These costs include initial capital equipment cost, operating and maintenance cost and energy cost. Another example is the comparison of the cost of materials that need to be coated to give satisfactory performance versus the cost of materials that do not need to be coated. The initial cost of coating is usually included in the evaluation of such an alternative, but the cost of maintaining or periodically removing and replacing the coating are frequently ignored or underestimated. In many cases, the area to be recoated must be encapsulated to contain the removed coating and contaminated blast media and to achieve an environment (possibly by dehumidification) that is required for proper coating application. If these types of system considerations are not properly addressed, incorrect cost-based materials selection decisions are likely.

Schedule is frequently a very important factor in a system. Materials that have long lead times for delivery are likely to have an adverse affect on schedule. In some cases, the economic benefits from meeting a schedule for system completion will outweigh increases in life-cycle costs due to use of materials that are immediately available but have a higher life-cycle cost.

Matching Design to Materials Performance

In many cases, particularly if materials and design are considered concurrently in the design process, designs can be modified to accommodate material properties.

Designing for a Specific Material

Design codes are commonly specific to a material or group of similar materials. These design codes usually only consider mechanical design factors such as strength and toughness and usually do not consider factors such as corrosion resistance.

When, at least tentative, material property requirements have been established, the designer must then determine which candidate materials have the required properties. It is important at this stage to use realistic materials properties. Materials properties are commonly given as maximum, minimum or typical properties. Selection of a material where the maximum available property just meets the system requirement will usually result in high costs due to the level of quality control required as well as the use of special fabrication techniques required to maintain the maximum material properties. This is particularly true when welding will be used for fabrication. On the other hand, most actual material properties exceed the minimum properties by a substantial margin. In some cases, material producers will supply materials with properties substantially superior to the commonly listed minimum values and will certify the material to the higher actual properties. This is particularly true when large amounts of material are required. It is important that the designer and material producers maintain a dialogue regarding what the producer can supply.

Fabrication considerations are an important factor in selecting materials. Most commercial metals and alloys can be welded. However, this welding varies considerably in difficulty and cost and may adversely affect the properties of the base materials. Welding processes and costs for shop fabrication, field fabrication, and repair must be considered in order to make appropriate

materials selections. Some materials, such as titanium, require very specialized welding process. While there are many shops that can handle these special considerations, field welding and field weld repair of these materials can be difficult and expensive and these must be considered in order to make appropriate materials selections. Thus, the welding engineer must be an integral part of the design team in order to make appropriate material selection decisions during the design process.

Avoiding Undesirable Design Features

In the design process, features that encourage corrosion can usually be avoided. Some of these features are common to all materials and some result in increased corrosion of only selected materials. If the structure is to be coated, other types of features must be avoided.

In atmospheric exposures, any material that is not completely resistant to corrosion will be affected by time of wetness. Features such as those that collect and hold water and debris should be avoided if corrodable materials are being considered. These features not only increase the time of wetness, but the debris can either by directly chemically reactive or may foster the growth of organisms that produce corrosive byproducts. In some cases, these features can be avoided by simple re-orientation, or by adding holes for drainage.

Some materials such as the stainless steels and nickel alloys have better corrosion resistance when there is a continuous supply of oxygen to their surfaces than when the supply of oxygen is inhibited. The availability of oxygen can be inhibited by trapped debris or in crevices formed between adjoining surfaces. Inhibition of oxygen access by debris can be avoided as above. Crevices can be eliminated through the use of welded joints that completely eliminate the crevices. In many cases, an alloy with insufficient corrosion resistance in the presence of adverse design features will perform satisfactorily if these features are eliminated by design. When crevices cannot be eliminated by design, resistance to crevice corrosion becomes a very important factor in the selection of materials.

If the system is to be coated, other factors must be considered during design. These include access to the surfaces to be coated for both surface preparation and coating application. The surfaces to be coated must be smooth and free from contaminants such as weld spatter. Welds and other rough features must be ground smooth to prevent uneven coating thickness. Corners and edges must be treated to avoid features that result in uneven coating thickness. Areas where the coating is thin will not receive adequate protection and where the coating is thick it may not cure properly or may crack due to shrinkage during curing.

Figure 4 illustrates some of the factors that can affect corrosion and coating performance and suggestions for design alternatives.

11
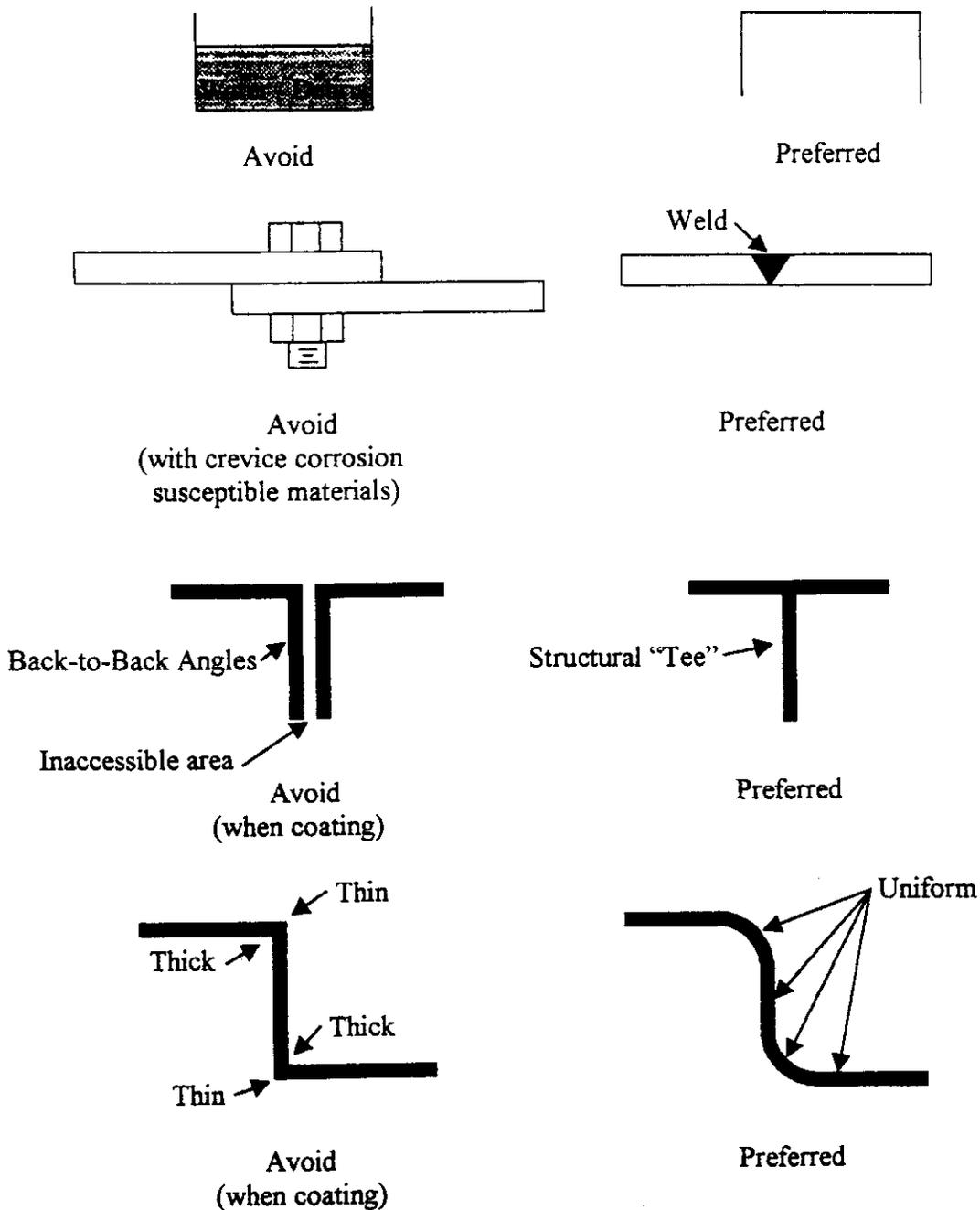
Figure 4. Design details that affect corrosion and design alternatives.

The Role of the Materials Industry in Meeting Materials Challenges

The materials industry has a significant role in meeting materials challenges. New materials will be developed to meet materials requirements. New applications for existing materials will be identified. A primary role of the materials industry is the transfer of information on materials performance to the marine industry and maintaining a dialogue with the marine industry regarding potential materials applications.

Developing New Materials

It is likely that new materials will be developed specifically to meet marine application requirements. However, the market for marine materials is smaller than other markets such as land-based structures, transportation equipment, aerospace, or the chemical process and petrochemical industries. Thus it is likely that more materials will be developed for these other applications than for marine markets. However, materials developed for these other markets may have potential marine applications.

Materials producers are constantly striving to increase the demand for their materials. Most materials producers have marketing groups that review potential applications for both newly developed and currently produced materials. In some cases, this marketing function is also performed by trade associations such as the Aluminum Association, The American Iron and Steel Institute, the Copper Development Association, the International Titanium Association, and the Nickel Development Institute. These groups are supported by their respective materials producers and augment in-house market development efforts. Identification of potential marine applications for materials begins with the establishment of a dialogue between the end users and materials industry representatives. Problems with existing materials and plans for new applications having new materials requirements are identified through these dialogues. Candidate materials are identified and the materials industry representatives and end users work together to evaluate newly identified applications.

One vital step in this process is the characterization of the performance of the material in marine applications. While many performance characteristics such as strength and ductility are common to all applications, the characterization of corrosion performance in marine environments must be determined separately. Laboratory screening tests are useful in identifying materials that have good potential for marine applications. However, actual marine environment exposure is usually required to validate the marine corrosion characteristics of a material. These in-situ tests usually require several years of exposure in both atmospheric and immersion conditions. Application related considerations such as crevices and stress must be included in the characterization of the material. These evaluations are both costly and time consuming and are usually performed only on those materials that are considered to have good potential for marine applications.

Providing Material Property Information

The materials industry provides the marine industry information on the performance of materials in many ways. Publications by materials producers and trade associations are a valuable source of this information. The materials industry also disseminates information on materials properties and potential applications through technical presentations at professional societies, marine trade associations and directly to the end-users. It is vital that this disseminated information be factual and unbiased. It is in the interest of the materials industry to insure that applications of their materials are indeed cost-effective and appropriate. A single material failure due to

13

inappropriate information can be very costly with regards to future applications. In addition, if it is found that a material is not as cost effective for an application as was initially projected, the opportunity for future applications of that material will be restricted.

Assisting With Materials Applications

The materials industry also works directly in assisting the marine industry in the efficient and cost effective application of their materials. Through the dialogue between the materials industry and the marine industry both failures and successes can be identified and transferred to new applications through the dissemination of "lessons learned". The materials industry can also assist the marine industry in the areas of fabrication, inspection and maintenance. Optimization of materials applications can occur only with a partnership between the materials industry and the marine industry.

Summary

There are many challenges facing both the producers and users of materials. The ultimate goal of both groups is to optimize the selection of materials in terms of obtaining satisfactory system operation at the lowest life-cycle cost. This goal can be best achieved when the materials and marine industries to work together to optimize materials applications.

Metallic Coatings for Corrosion Control of Marine Structures

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Abstract

The use of metallic coatings including copper-nickel alloys, nickel-copper and stainless steel, particularly in the spray/splash zone, is a proven and valuable engineering method for corrosion protection of marine structures. The excellent performance of the copper-nickel alloys in terms of both corrosion and biofouling resistance in marine environments suggests these alloys for the protection of offshore structures and ship hulls. Sheathing techniques have been developed for both applications and some service experience has been gained on 90-10 copper-nickel (C70600), 70-30 copper-nickel (C71500) and 70-30 nickel-copper (Alloy 400). Furthermore, 70-30 nickel-copper (Alloy 400) sheathing has been utilized on legs and risers of oil and gas platforms in several parts of the world. This paper reviews the properties of the copper-nickel alloys including the corrosion behavior and biofouling resistance as affected by composition, water velocity, exposure conditions and methods of attachment to steel. The mechanisms of offshore structure corrosion are reviewed, leading to discussion of the most effective use of a copper-nickel protective sheath. Results of a number of long term trials of copper-nickel alloys applied to pilings as well as ship hulls are described. Cost benefits due to reduced maintenance and to reduced structure size and weight through elimination of splash zone corrosion allowance and to lower wave forces on the structure have been analyzed. Methods of application of copper-nickel alloy sheet to platform structural members, and alternative resin-particulate containing copper-nickel sheet formulations are discussed.

Key terms: seawater corrosion, copper-nickel alloys, nickel-copper alloys, stainless steels, metallic coatings, offshore structures, biofouling

Introduction

Marine engineers have long sought effective and economical means to protect structures from the ravages of seawater corrosion and marine biofouling. A broad range of coating systems, some with antifouling properties, have been developed and are the most commonly used approach to protecting steel structures, ship hulls in steel, wood, glass fiber reinforced plastics (GRP) and aluminum, as well as concrete, wood pilings, etc. Coatings will of course continue to be used including the cupric oxide and organotin antifouling paint systems although the latter has been banned in many countries because of their high toxicity to marine life. Where extremely long life with freedom from maintenance is required, use of metallic sheathing has proved to be a sound engineering approach. A variety of alloys including stainless steels, 70-30 nickel-copper (Alloy 400) and the copper-nickel alloys have been applied. The copper-nickel alloys are particularly attractive for marine structure sheathing because they provide corrosion protection and at the same time resist the build up of the thick biofouling mass that degrades the performance, structural integrity, and even the safety of the structure. In addition, copper-nickel alloys reduce maintenance costs by minimizing the need to remove biofouling on a regular basis as well as eliminating the need for periodic reapplication of biofouling-resistant paints and coatings.

This paper first briefly reviews the properties of the copper-nickels and nickel-copper (Alloy 400) that recommend them for use as sheathing materials. It then discusses galvanic effect issues arising due to the relatively noble sheathing alloys in contact with the steel structures and finally describes a number of successful installations and sheathing systems applicable to offshore structures or to ship hulls.

The Copper-Nickel Alloys

Alloy Compositions

Of the several copper-nickel alloys, two alloys are extensively used in marine applications including piping, condensers and desalination plants; the 90% copper-10% nickel (90-10) alloy and the 70% copper-30% nickel (70-30) alloy. These are denoted C70600 and C71500 respectively in the Unified Numbering System used in the United States and Canada. Both alloys contain iron and manganese additions to improve impingement and localized corrosion resistance. Manganese additionally functions as a deoxidizer and is intentionally added for that purpose when the alloy is being melted. When comparing the various specifications used worldwide, the compositional ranges of the two alloys vary slightly from one specification to the next, as shown in Table I.

TABLE I
COMPARISON BETWEEN VARIOUS SPECIFICATIONS FOR 90-10 AND 70-30 COPPER NICKEL ALLOYS
(Maxima except where range given)

		90-10			
		ISO	BS	ASTM	DIN
		CuNi10Fe1Mn	CN 102	C70600	CuNi10Fe 2.0872
Copper	min	Rem	Rem	Rem	Rem
	max				
Nickel	min	9.0	10.0	9.0	9.0
	max	11.0	11.0	11.0	11.0
Iron	min	1.2	1.0	1.0	1.0
	max	2.0	2.0	1.8	1.8
Manganese	min	0.5	0.5	-	0.5
	max	1.0	1.0	1.0	1.0
Tin	min	-	-	-	-
	max	0.02	-	-	-
Carbon		0.05	0.05	0.05*	0.05
Lead		0.03	0.01	0.02*	0.03
Phosphorus		-	-	0.02*	-
Sulphur		0.05	0.05	0.02*	0.05
Zinc		0.5	0.5	0.5*	0.5
Total Other Impurities		0.1			0.1
Total Impurities		-	0.3	-	-

		70-30			
		ISO	BS	ASTM	DIN
		CuNi30Mn1Fe	CN 107	C71500	CuNi30Fe 2.0882
Copper	min	Rem	Rem	Rem	Rem
	max				
Nickel	min	29.0	30.0	29.0	30.0
	max	32.0	32.0	33.0	32.0
Iron	min	0.4	0.4	0.4	0.4
	max	1.0	1.0	1.0	1.0
Manganese	min	0.5	0.5	-	0.5
	max	1.5	1.5	1.0	1.5
Tin	min	-	-	-	-
	max	0.02	-	-	-
Carbon		0.06	0.06	0.05*	0.06
Lead		0.03	0.01	0.02*	0.03
Phosphorus		-	-	0.02*	-
Sulphur		0.06	0.08	0.02*	0.05
Zinc		0.5	0.5*	0.5	
Total other Impurities		0.1			0.1
Total Impurities		-	0.3	-	-

*When required for welding

These variations have little influence on the service performance of the alloys. Iron is essential for both 90-10 and 70-30 copper nickel because it provides added resistance to erosion-corrosion caused by moving seawater, which is especially important to pipe systems. These two elements, iron and to a lesser extent, manganese, increase the shear force (from the flowing seawater) required to remove the protective oxide. The beneficial effect of iron content on the impingement attack on 90-10 copper-nickel from 30-day tests at 3 m/s water velocity has been verified.[1] A distinct minimum is apparent between 1.5 and 2.5% iron. It is generally believed that iron should be in solid solution to be effective and provide maximum impingement corrosion resistance; i.e., the material must be cooled relatively rapidly after hot rolling or annealing. However, impingement corrosion is not a large issue in sheathing applications and therefore whether or not the iron is in solution is not a concern. The composition of 70-30 nickel-copper (Alloy 400) is given in Table II.

TABLE II

COMPOSITION OF 70-30 NICKEL-COPPER (ALLOY 400) - IN WEIGHT %*
(Maxima except where range given)

Nickel	
min	63.0
Copper	
min	28.0
max	34.0
Iron	2.
Manganese	2.0
Carbon	0.3
Sulfur	0.024
Silicon	0.5

*Specifications Include UNS N04400; ASTM B127, B 163-B165, B 564; DIN 17743, 17750-17754, BS 3072-3076 (NA 13)

Mechanical Properties
Typical annealed mechanical properties of the two copper-nickel alloys and the one nickel-copper alloy are shown in Table III.

TABLE III

TYPICAL MECHANICAL PROPERTIES OF COPPER-NICKEL AND
NICKEL-COPPER ALLOY 400
(As Hot Rolled)

Property	90-10	70-30	Alloy 400
Yield Strength, MPa (0.5% ext.)	110	138	240*
Tensile Strength, MPa	303	379	550
Elongation, %	42	45	40

* 0.2% offset

Strength increases with nickel content. These three alloys are single phase, solid solution strengthened and are not hardenable by heat treatment. Strength can be increased by work hardening and is an effective means of strengthening drawn products such as tube, rod or wire. A smaller amount of strengthening by cold work is possible for the wide plate required for ship hull or offshore structure sheathing and can be helpful in regard to durability.

The high strength and ductility of the copper-nickel alloys give assurance that a sheathed steel jacket member will withstand normal impact, erosion and abrasion that might be experienced in service operations on a platform.

Corrosion Resistance

Metals and alloys are subject to several forms of corrosion in seawater including general wastage, impingement attack and localized corrosion, such as pitting, crevice corrosion, stress corrosion cracking and intergranular attack. The continued use of copper-nickel in alloys over many years in seawater has confirmed their good resistance to the wide variety of these forms of corrosive attacks.

General Corrosion. General corrosion rates for 90-10 and 70-30 copper-nickel alloys in seawater are low, ranging between 0.025 and 0.0025 mm/yr[2]. For the majority of applications, these rates would allow the alloys to last the required lifetime, and there would be little probability of their premature failure in service due to such a corrosion mechanism.

Fourteen years of data collected at the LaQue Center for Corrosion Technology at Wrightsville Beach, North Carolina USA, for 90-10 and 70-30 alloys[3] in quiet seawater, flowing seawater (0.6 m/s), and tidal conditions are shown in Figure 1.
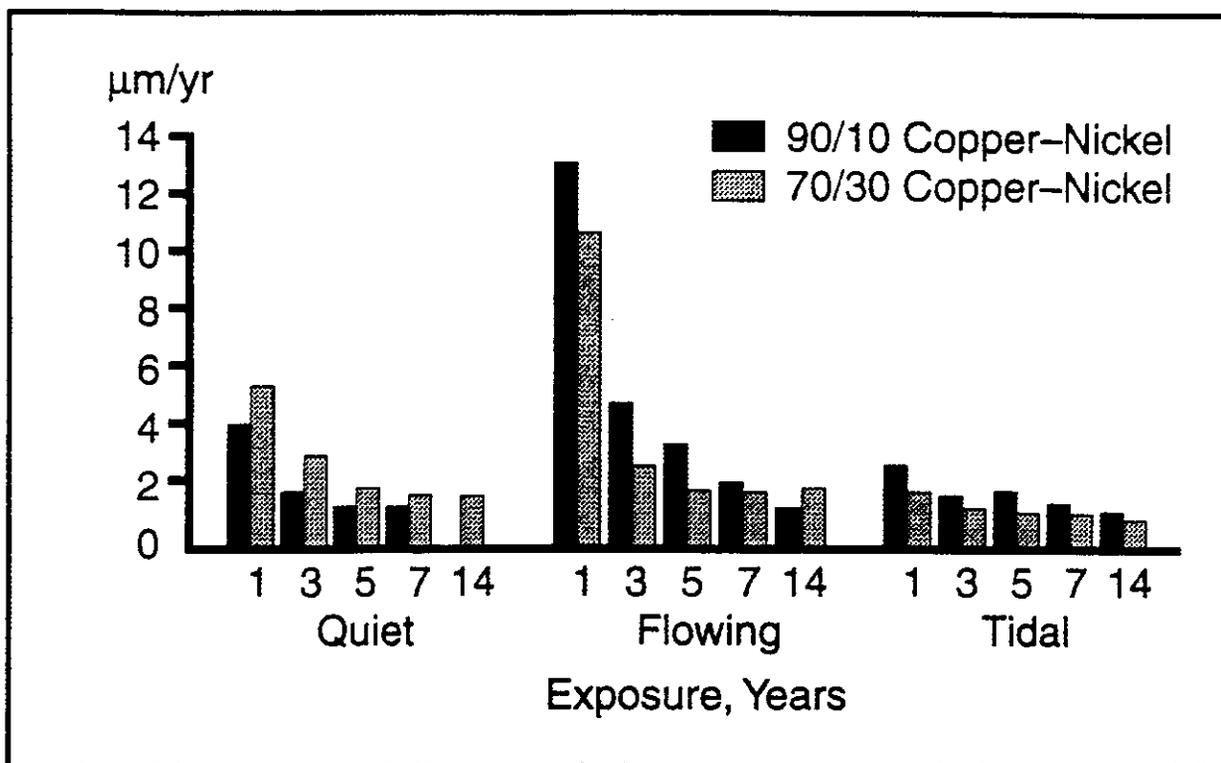
Figure 1   The change in corrosion rate with time for 90-10 and 70-30
            Copper-nickel in quiet, flowing and tidal zone seawater.

It was found that, in all instances, corrosion rates were higher during early stages of testing, before stabilizing of their protective corrosion films and then decreases as these films mature. The highest initial corrosion rates were found in flowing seawater; although in the latter years of testing, the corrosion rates for 90-10 were similar in all the conditions. For 70-30 copper-nickel, this trend of decreasing corrosion rates with increasing time, was true for quiet as well as flowing conditions, but corrosion rates were consistently lower for tidal conditions throughout. In summary, both alloys exhibit parabolic film growth and low general corrosion rates.

Localized Corrosion. Alloys, such as stainless steels, are protected by a passive film and tend to have low general corrosion rates. However, they can suffer localized corrosion once their films are damaged. This occurs in susceptible alloys, particularly at velocities of less than 1 m/s when marine-fouling attachments can form additional crevice sites. At higher velocities, marine organisms have difficulty becoming attached.

Copper-nickels have advantages over some other alloy types by having a high resistance to biofouling, thereby decreasing the number of potential sites where localized corrosion could occur. The copper-nickels also have a high inherent resistance to pitting and crevice corrosion in quiet seawater. Sixteen-year tests[4] on 70-30 copper-nickel alloy reported the average depth of the twenty deepest pits to be less than 0.127 mm. When pits do occur, they tend to be shallow and broad in nature and not the undercutting type of pitting which can be expected in some other types of alloys.

Crevice corrosion seldom occurs in copper-nickel alloys and little data is published about the phenomenon.[1]

The copper-nickels are generally immune to chloride-and sulphide-stress corrosion cracking in seawater and have a high resistance to stress corrosion cracking due to ammonia in seawater service.

Galvanic Effects. Copper-nickel alloys are fairly central in the galvanic series. They are: less noble than titanium, nickel-copper alloys and stainless steels; compatible with other copper-based alloys; and more noble than steels. The 70-30 copper-nickel alloy is slightly more noble than the 90-10 alloy. Therefore the 70-30 copper-nickel alloy is frequently used as the weld filler metal in welding the 90-10 alloy.

Protective Film Formation. The good corrosion resistance in seawater offered by copper-nickel alloys is a direct consequence of the formation of protective oxide films on their metal surfaces. These films form naturally and quickly following the initial exposure of these alloys to seawater.

In clean seawater, the film is predominantly cuprous oxide, and its protective value is enhanced by the presence of nickel, iron and manganese. Cuprous hydroxy-chloride and cupric oxide are often also present.[4,5] The film can be brown, greenish-brown or brownish-black. In 90-10 copper-nickel, the film thickness can be on the order of 4400 A.[1,5]

The rate of film formation was characterized by Tuthill[5], from the measurements of the copper content of condenser seawater effluent, over a three-month period after start up. Copper content was found to decrease from 10 to 1 ppm in ten minutes and further to 0.1 ppm in an hour. After three months, the copper in the effluent was at virtually the same level as that in the intake water, which is below 0.01 ppm. This indicates that the growth or maturation of the protective film, over time results in a reduction in the corrosion rate of the 90-10 copper-nickel condenser alloy tube surfaces.

The film, however, continues to become even more protective with time, as indicated by corrosion rate measurements made over several years. Studies in quiet seawater show that the time span approaches four years before the decrease in corrosion rate becomes negligible. In flowing water, the corrosion rate, as shown in Figure 1, was found to decrease continually over at least a 14-year period, the effect being similar for both 90-10 and 70-30 copper-nickel alloys. The composition and properties of the film depend on the alloy composition and the condition of seawater at the time of initial exposure. In polluted seawater, any sulfides present can interfere with film formation, producing a black film containing cuprous oxide and sulphide[1]. This film is neither as protective nor as adherent as films formed in unpolluted water. However, if an established cuprous oxide film is present, periodic exposure to polluted water can be tolerated without damage to the protective film.

Effect of Velocity. The combination of low general corrosion rates and high resistance to pitting and crevice corrosion ensures that the copper-nickel alloys will perform well in quiet,

clean seawater. As the flow rate of seawater increases, the corrosion rate remains low due to the adherent protective surface film on the alloys. However, once the velocity reaches a critical level, where the shear forces are sufficiently high to cause damage to the protective corrosion film, active underlying metal is exposed. This allows erosion-corrosion or impingement attack to occur. The seawater velocity at which this occurs is often called the "breakaway velocity" and different copper-based alloys show different breakaway velocities, as shown in Figure 2 prepared by Gilbert[6].
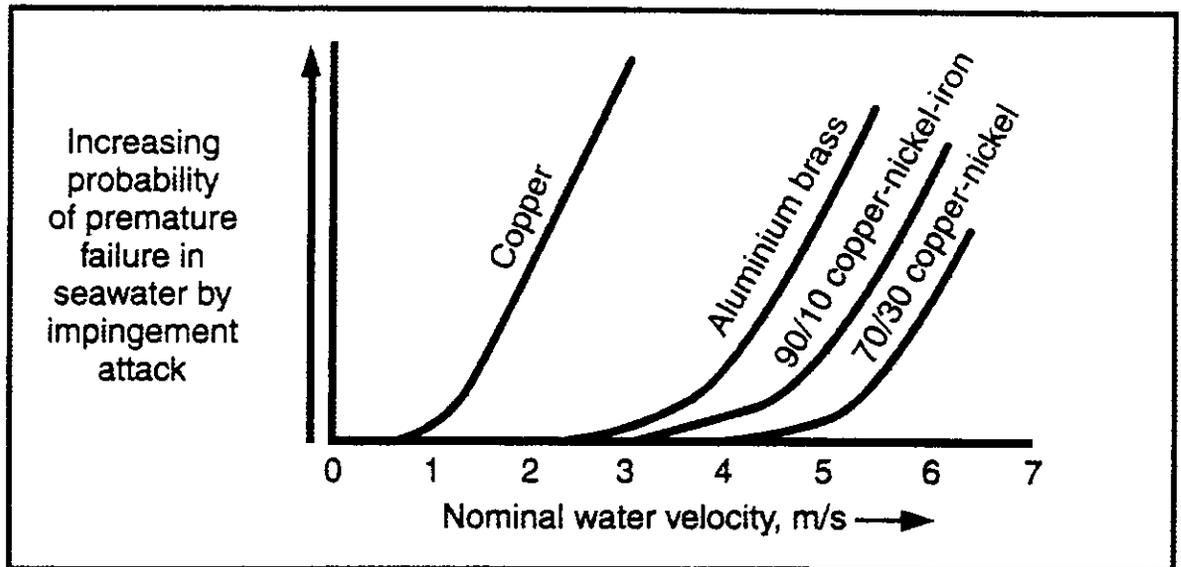
Figure 2   Velocity limitations for copper alloys in seawater.

Impingement corrosion is not a problem with copper-nickel alloys on fixed structures in seawater. Even with ship hulls protected with copper-nickel where the top speed significantly exceeds the nominal breakaway velocity of the 90-10 alloy, no erosion corrosion has been observed.[7,8,9] This is consistent with experiments done on larger diameter (102 mm) 90-10 copper-nickel pipe.[10] Resistance to seawater velocity of 7.3 m/s (the highest level obtainable in the experiment) was observed. This is consistent with the understanding of reduced shear stress at the pipe wall with increased pipe diameter at a given velocity. A planar ship hull can be viewed as a pipe of near infinite diameter.

Biofouling

Marine biofouling is commonplace in open waters, estuaries and rivers. It is commonly found on marine structures including pilings, offshore platforms, boat hulls, and even within piping systems and condensers. Fouling is usually heavier and more widespread in warm conditions and at low velocity (<1 m/s) seawater. At velocities above 1 m/s, most fouling organisms have difficulty attaching themselves to surfaces unless already secured. There are various types of fouling organisms including plants such as slime algae and sea mosses, sea anemones, as well as barnacles and mollusks such as oysters and mussels. On steel, polymers, and concrete marine construction, biofouling can be a very severe problem, resulting in unwanted excess drag on structures and marine craft in seawater, high wave loading on fixed

structures such as pilings, or blockages in pipe systems. Expensive removal by mechanical means is often required. Alternatively, costly prevention methods are employed, which include chlorination of piping systems or antifouling coatings on structures.

Marine organisms attach themselves to some metals and alloys more readily than they do to others. Steels, titanium and aluminum will foul readily. Copper-base alloys, including copper-nickel, have very good resistance to biofouling, and this property is used to advantage. In the case of copper-nickel, it is used to minimize biofouling on intake screens, seawater piping systems, water boxes, cladding of pilings and mesh cages in fish farming. A prime verification of the biofouling resistance of copper-nickel and alloys came to light in 1987 when two early copper-nickel hulled vessels, the *ASPERIDA II* and the *COPPER MARINER*, were located after being in service for 21 and 16 years, respectively. Neither vessel required hull cleaning nor had suffered significant hull corrosion during that time.[7]

The 70-30 alloy is used in marine applications where its higher strength is an advantage; e.g., the seawater piping systems in deep diving submarines or often in fire protection systems. Its biofouling resistance is marginally less than that of the 90-10 copper-nickel composition. The 90-10 copper-nickel has the best combinations of corrosion, velocity induced erosion and biofouling resistance and is the preferred alloy for protection of marine structures. Due to its lower nickel content, the 90-10 alloy is of course less costly as well. The 70-30 copper-nickel is more costly, but has somewhat higher velocity induced erosion resistance than the 90-10 alloy. The 70-30 nickel-copper (Alloy 400) is much less resistant to fouling than the copper-nickels due to its lower copper content of 30%.

Sheathing and Offshore Structures
Experience with Ship Hulls
As noted above, the use of copper-nickel to provide a corrosion and biofouling resistant ship hull has been extensively utilized on scores of boats of a variety of hull constructions. The most publicized is the 22-m shrimp trawler *COPPER MARINER* built for the Nicaraguan Ministry of Fishing in 1971[7]. This boat has a 6 mm-thick 90-10 copper-nickel hull and is still in service. The hull has never required maintenance. Solid copper-nickel hulls are practical for boats on this order of size. In large oceangoing freighters or tankers where a corrosion and biofouling resistant hull would markedly improve fuel economics and reduce maintenance costs, some practical means of applying a relatively thin layer of copper-nickel to the steel hull is needed. *COPPER MARINER II* and a series of fire boats[11] were built using copper-nickel clad steel; i.e., a composite material having a metallurgical bond between the steel and copper-nickel alloy. These boats have been very successful, but the clad steel may be too expensive for widespread utilization. An alternative is to sheath the ship or structure. Sheathing refers to the attachment of relatively thin copper-nickel plate to the steel by welding, adhesives, or in the case of offshore jacket structure members, by mechanical methods such as clamping or screwing in place, often with an electrical insulation material between the steel and the copper-nickel. Examples of these methods are discussed below.

Offshore Structures
Both the fouling resistance and corrosion protection aspects of copper-nickel sheathing are critical to protecting offshore structures. The attachment and growth of marine organisms

can add considerable weight to a structure; but more importantly, the increase in side loads on the structure due to currents, wind and waves is a major design consideration. Marine growth as thick as 0.7 to 1.2 m has been seen. Excessive marine growths extend frequently to about 1 m above mean sea level to about 10 meters below. Very large amounts of extra steel structure must be provided to resist the resulting forces. Regular and expensive removal of marine growth by divers using high pressure water is also required. As will be discussed below, sheathing can reduce these costs dramatically and provide overall savings to the platform owner.

Corrosion and Protection of Steel Structures in Sea Water. The intensity of corrosion of an unprotected steel structure in seawater varies markedly with position relative to the mean high and low tide level as shown in Figure 3.
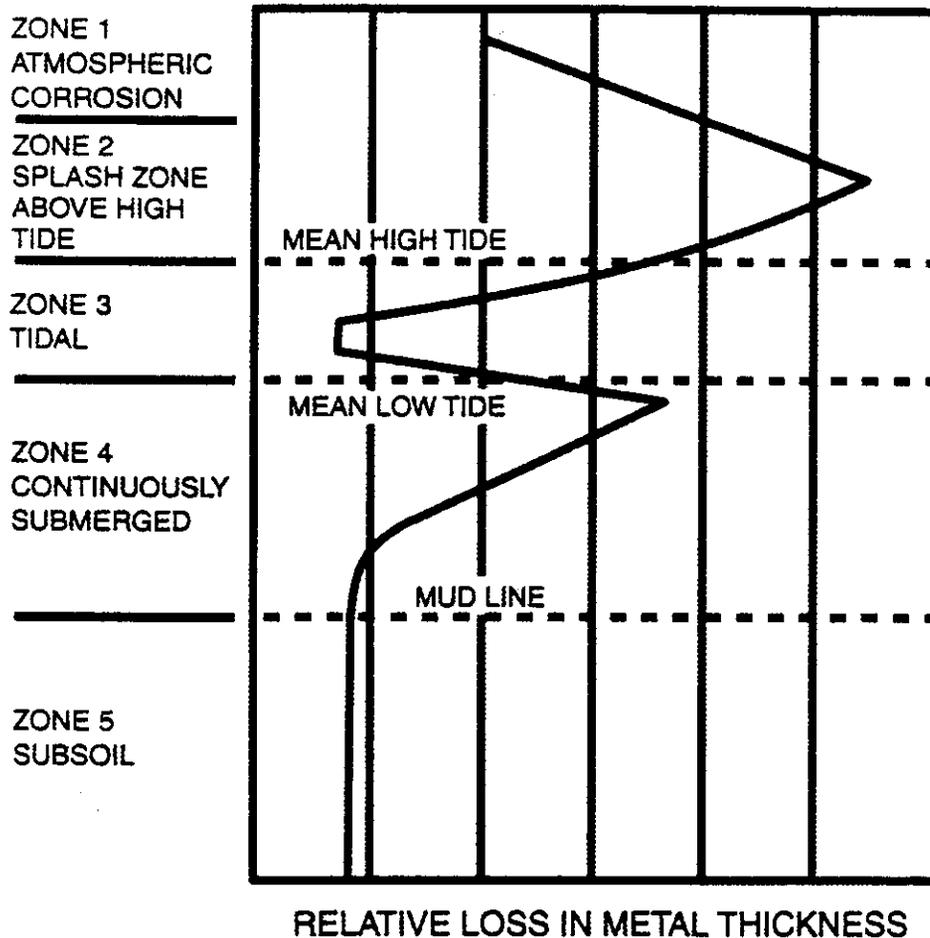
Figure 3   Profile of the Thickness Loss Resulting from Corrosion of an
            Unprotected Steel Structure in Seawater.

The spray and splash zone above the mean high tide level is the most severely attacked region due to continuous contact with highly aerated sea water and the erosive effects of spray, waves and tidal actions. Corrosion rates as high as 0.9 mm/y at Cook Inlet, Alaska, and 1.4 mm/y in the Gulf of Mexico have been reported. Cathodic protection in this area is ineffective because of

lack of continuous contact with the seawater, the electrolyte, and thus no current flows for much of the time. Corrosion rates of bare steel pilings are often also very high at a position just below mean low tide in a region that is very anodic relative to the tidal zone, due to powerful differential aeration cells which form in the well aerated tidal region.

Protection of a steel structure can be affected by various means; each corrosion zone must be separately considered. Three generally accepted methods are cathodic protection, painting or coating, and sheathing. Sheathing has proved to be a very successful approach when applied in the region through the splash/spray zone to a short distance below the tidal zone. As early as 1949, 70-30 nickel-copper (Alloy 400) was utilized on an offshore platform in the Gulf of Mexico off the Louisiana coast[12,13].

Early Sheathed Piling Trials. The LaQue Center at Wrightsville Beach, North Carolina, USA, conducted extensive trials of sheathing using the steel piling which support the sea water corrosion test wharves at the laboratory as test specimens. Sheathing or protective materials tested included 70-30 nickel-copper (Alloy 400), 18-8 chromium-nickel AISI Type 304 stainless steel, 70-30 copper-nickel, and both nickel (Nickel 200)-clad and 70-30 nickel-copper (Alloy 400) clad on steel. All of these were reported to be performing very well after 39 years of exposure.[14]

A large number of proprietary coatings, including galvanizing and sprayed zinc and aluminum, were also tested; all proved to have finite effective lifetimes extending up to 13 years[15]. The 90-10 copper-nickel alloy was not included in these early sheathing trials because its composition with regard to iron and manganese was not yet established.

Directly Welded Sheaths-Galvanic Effects. In the early trials, the 70-30 nickel-copper (Alloy 400) and the 70-30 copper-nickel alloy sheaths were welded directly to the steel. One might assume that corrosion of the anodic steel below the tidal zone would be accelerated because it is in direct contact with the more noble sheathing alloy. A number of experiments were conducted at the LaQue Center to investigate this possibility[14]. On the contrary, steel below the tidal zone is found to be cathodic relative to the noble alloy sheathing material, since the sheathing alloy, which is 70-30 nickel-copper (Alloy 400) in this case, becomes polarized to the potential of the adjacent steel below. Hence the submerged steel below the sheathed piling corrodes at a lower rate than the submerged steel on an unsheathed bare steel piling because the resulting galvanic current between the sheathed tidal zone and the submerged steel below it is lower.

This conclusion is confirmed by the results of galvanic corrosion tests conducted to determine the effects on submerged steel coupled to other alloys in the tidal zone[15], as shown in Figure 4.
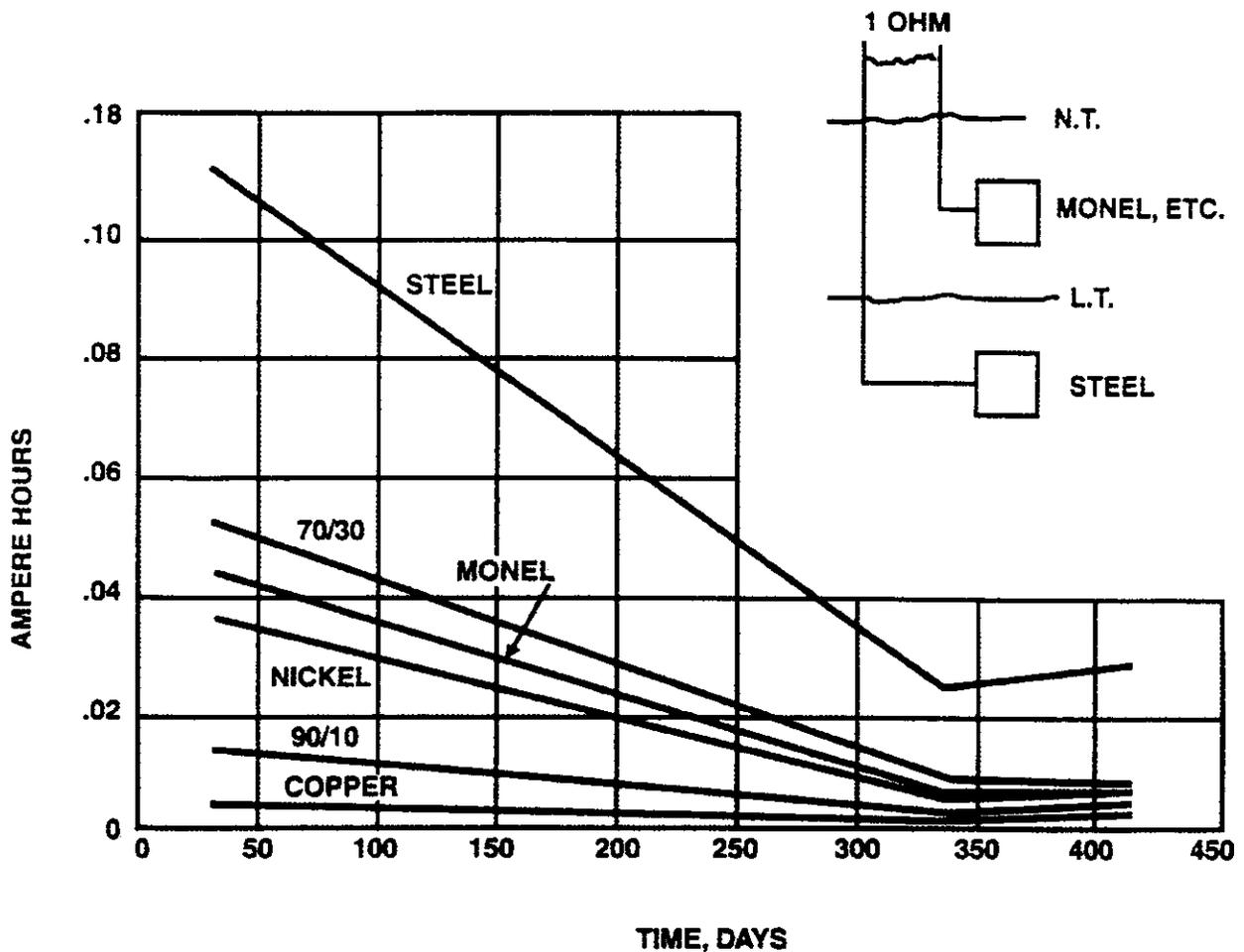
Figure 4   Total Current per Tide vs. Time between Plates in a Simulated
            Piling Test.

Plates of the alloys placed in the tidal zone are coupled to submerged steel plates, and the total current per tide was measured periodically over the 14-months of exposure. Current decreased with time, but the results demonstrated clearly that the most severe galvanic couple is steel to steel. Although the potential difference between the noble alloy-to-steel couples is significantly greater than the potential difference between two steel panels, the rapid and nearly complete polarization of the noble metal results in a lower galvanic current. More recently, the International Copper Research Association (now the International Copper Association) conducted several research programs clarifying and elaborating on these earlier findings[16,17,18]. In summary, steel under water corrodes less when in contact with noble metals in the tidal zone than when coupled to another panel of steel in the tidal zone.

As discussed above, the 90-10 copper-nickel alloy provides the best combination of corrosion resistance and biofouling protection. Attachment of this sheathing material to the steel structure by welding or mechanical fasteners will result in cathodic polarization of the sheath material and somewhat of a reduction in the antifouling capability of the 90-10 copper-nickel

alloy. Therefore it is necessary to electrically insulate the sheath from the steel jacket members to gain the full advantage of the biofouling resistance properties of the alloy. Electrical insulation can be achieved by pumping cement or an epoxy into the annular space between the component and the sheath or, more simply, by use of an elastomer or rubber-base insulator. The copper-nickel can be in the form of sheet, wire grid, particles or flame-sprayed coatings. Bonding of the steel-elastomer-copper-nickel interfaces can be by vulcanizing, by the use of epoxy adhesives, by mechanical means or a combination of methods. Estimated costs of sheathing ranged from $194 to $322 per square meter ($18 to $30 per square foot).[19]

More Recent Sheathed Piling Tests. Long term exposure of copper-nickel sheathed steel pilings, to assess the effectiveness of corrosion and biofouling resistance as well as the cathodic protection systems in several configurations as described below was sponsored by the International Copper Association and the Copper Development Association Inc. and carried out at the LaQue Center in Wrightsville Beach, North Carolina. USA[20,21]. Over 50 ASTM Type A-36 steel pilings 17 cm in diameter were sheathed with 4.6 mm thick x 3 m long 90-10 copper-nickel. Some copper-nickel sheaths were directly welded to the steel, others were insulated from the steel with concrete or with 6 mm of a butyl rubber compound. Some piling were cathodically protected with Galvalum III anodes while others remained unprotected. Pilings were removed after two years, five and ten years of exposure in a natural flowing seawater channel for evaluation.

The results of biofouling accumulations on these pilings are summarized in Table IV.

TABLE IV

BIOFOULING MASS ON 90-10 COPPER NICKEL SHEATHED STEEL
PILINGS AFTER FIVE AND TEN YEARS

Piling	kg/m²	Percent	Biofouling Organisms
Bare Steel*			
5 years	18.00	100.0	massive barnacles, oysters, etc.
10 years	12.00	100.0	
Concrete-Insulated Cu-Ni on Steel			
5 years	0.36	1.9	only scattered barnacles
10 years	0.14	1.2	
Cu-Ni Directly Welded to Steel			
5 years	7.95	44.3	moderate barnacles, oysters, etc.
10 years	4.43	36.8	
Rubber-Insulated Cu-Ni on Steel			
5 years	0.26	1.4	scattered barnacles, oysters, etc.
10 years**	0.51	4.2	
Rubber-Insulated Cu-Ni on Steel w/Galvanic Couple (single point contact)			
5 years	4.59	25.5	moderate barnacles, oysters, etc.
10 years***	15.39	37.0	

*   unsheathed - experimental control
**   average value (3 pilings)
*** average value (2 pilings)

Organisms observed include barnacles, oysters, codium, tunicate, colonial tunicate, encrusting and filamentious bryozoans but not all were present on all pilings, as shown in Table IV. After five years the mass accumulated on the bare steel piling was more than twice as great as that which accumulated on the directly welded 90-10 copper-nickel piling and more than 50 times higher than the average amount that attached to the concrete and rubber insulated sheathing. Only a few scattered barnacles were seen on the concrete insulated copper-nickel sheath after five years. After ten years the unsheathed bare steel is still heavily fouled but its fouling mass is somewhat reduced. However, the fouling mass of the rubber insulated pilings shows an increase over time while the concrete insulated pilings show a decrease when the five and ten year results are compared. The variability in fouling mass over time are normal, especially when one considers that this is a field test and therefore not conducted under controlled laboratory conditions. It is reasonable to assume that the two hurricanes that came ashore in the area in 1996 reduced the total accumulation of biofouling on heavily fouled pilings. All the sheathed pilings continue to resist fouling after ten years.

The galvanic anodes used on the cathodically protected piling were cleaned and weighed; mass loss and consumption rates are given in Table V.

TABLE V

GALVALUM III ANODE WEIGHT LOSS AND CONSUMPTION RATE
WHEN COUPLED TO 90-10 COPPER-NICKEL SHEATHED STEEL PILINGS

Piling Type	Weight Loss* grams	Consumption Rate kg/yr
Bare Steel**		
2 years	716.4	0.36
5 years	1880.6	0.36
10 years	2316.1	0.23
Concrete-Insulated Cu-Ni on Steel		
2 years	755.3	0.38
5 years	1256.6	0.25
10 years	181.8	0.04
Cu-Ni Directly Welded to Steel		
2 years	414.1	0.21
5 years	687.6	0.14
10 years	2050.8	0.21

*   combined weight - two anodes per piling
** unsheathed - experimental control

In the two-year exposures, the directly welded piling displayed a lower anode consumption rate than the bare steel; the concrete insulated consumption rate was comparable to that of the bare steel. After five years of exposure, both the directly welded and the concrete insulated pilings displayed reduced consumption rates. After ten years of exposure, the anode consumption rate of the directly welded copper-nickel on steel pilings returned to the rate initially observed after two years. This variability is also not unexpected when one considers that these are field exposures and are not conducted in a laboratory under controlled conditions. The reduction in anode consumption for the directly welded piling is considered to be due to the favorable polarization behavior of the 90-10 copper-nickel alloy. The reduced anode consumption rate for the concrete insulated piling is attributed to the high resistance path through the concrete to the underlying steel. The overall reduction in anode

consumption rates for both sheathing techniques could in part be due to the reduction in current resulting from calcareous film formation on the 90-10 copper-nickel alloy.

It was also observed that even in the case where the sheathing is directly welded to the steel and exposed without cathodic protection for five years, there was no grossly accelerated attack of the steel immediately above or below the sheath. The average corrosion rates in the steel adjacent to the sheathing below the mean low tide point did not exceed 0.25 mm/y, which is no higher than the corrosion rate of the freely corroding, unsheathed steel control pilings. Of course, exposure of any steel piling without cathodic protection is not recommended.

A second series of experiments were conducted at Kure Beach, North Carolina, USA, at an oceanfront site by the LaQue Center[22]. A total of six pilings were exposed to oceanfront wave action, three on the north side and three on the south side of a fishing pier, slightly offshore from the wave breaker line. Their biofouling mass was measured after ten years and is shown in Table VI.

TABLE VI

BIOFOULING MASS ON 90-10 COPPER NICKEL SHEATHED STEEL
PILINGS AFTER TEN YEARS OF EXPOSURE ON THE OCEANFRONT AT
KURE BEACH, NORTH CAROLINA, USA

Piling	kg/m^2
Bare Steel (north side)*	3.61
Bare Steel (south side)*	2.92
Directly Welded on Steel (north side)	2.34
Directed Welded on Steel (south side)	2.34
Concrete Insulated Steel (north side)**	1.56
Concrete Insulated Steel (south side)	0.59

*   unsheathed - experimental control
**   partially shorted

As expected, the bare steel experiment controls had the highest biofouling mass, which was 500% to 600% greater than the value obtained from one of the concrete-insulated pilings (south side). The biofouling mass on the other concrete insulated piling (north side) was two-thirds the average amount accumulated on the directly welded piling. Note that the large accumulation on the concrete insulated piling (north side) was attributed to it being partially electrically shorted and therefore is more representative of a directly welded rather than insulated sheathing. The biofouling mass of the directly welded piling was 65% to 80% of the amount which grew on the bare steel experimental control pilings. However, the fouling on the latter copper-nickel-directly welded-to-steel pilings, was poorly adherent and easily removed.

The Exxon Production and Research Company carried out a generalized economic evaluation[23] for the International Copper Research Association by means of a computer aided design study of a conventional steel structure as depicted in Figure 5.

GRAVITY LOADS
(DECK LOAD,
STRUCTURE WEIGHT)

BAY

ENVIRONMENTAL FORCES
(WAVE, WIND, CURRENT)

JACKET

PILES

CONDUCTORS
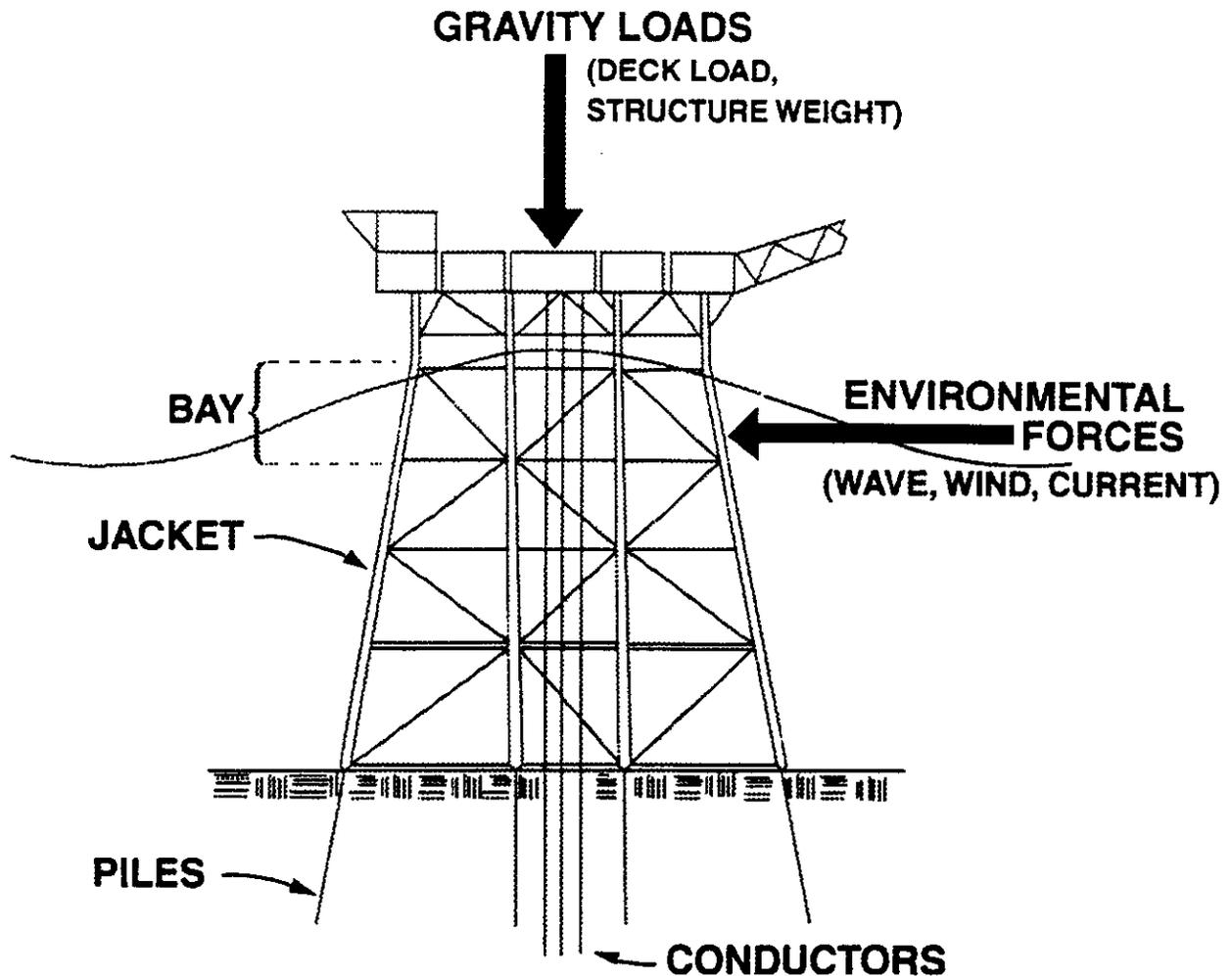
Figure 5   Simplified Diagram of Forces Acting on Off-shore Structures

Only insulated copper nickel alloy sheathing systems were considered as these gave the full economic benefits by minimizing of both marine fouling and corrosion. Design models were worked out for a range of situations, covering three different water depths, environmental conditions (wind, wave and current) ranging from mild to severe, and marine growth ranging from light to heavy. In all, 29 scenarios were considered. Potential cost savings were calculated based on the savings in weight of installed steel. The cost of the sheathing material and its installation were not included in the analysis, because of variability of the means of attachment and lack of data on these costs.

The gross savings for offshore structures per unit area of sheathing, which factors in all the total steel, fabrication and installation costs, are summarized in Figure 6.
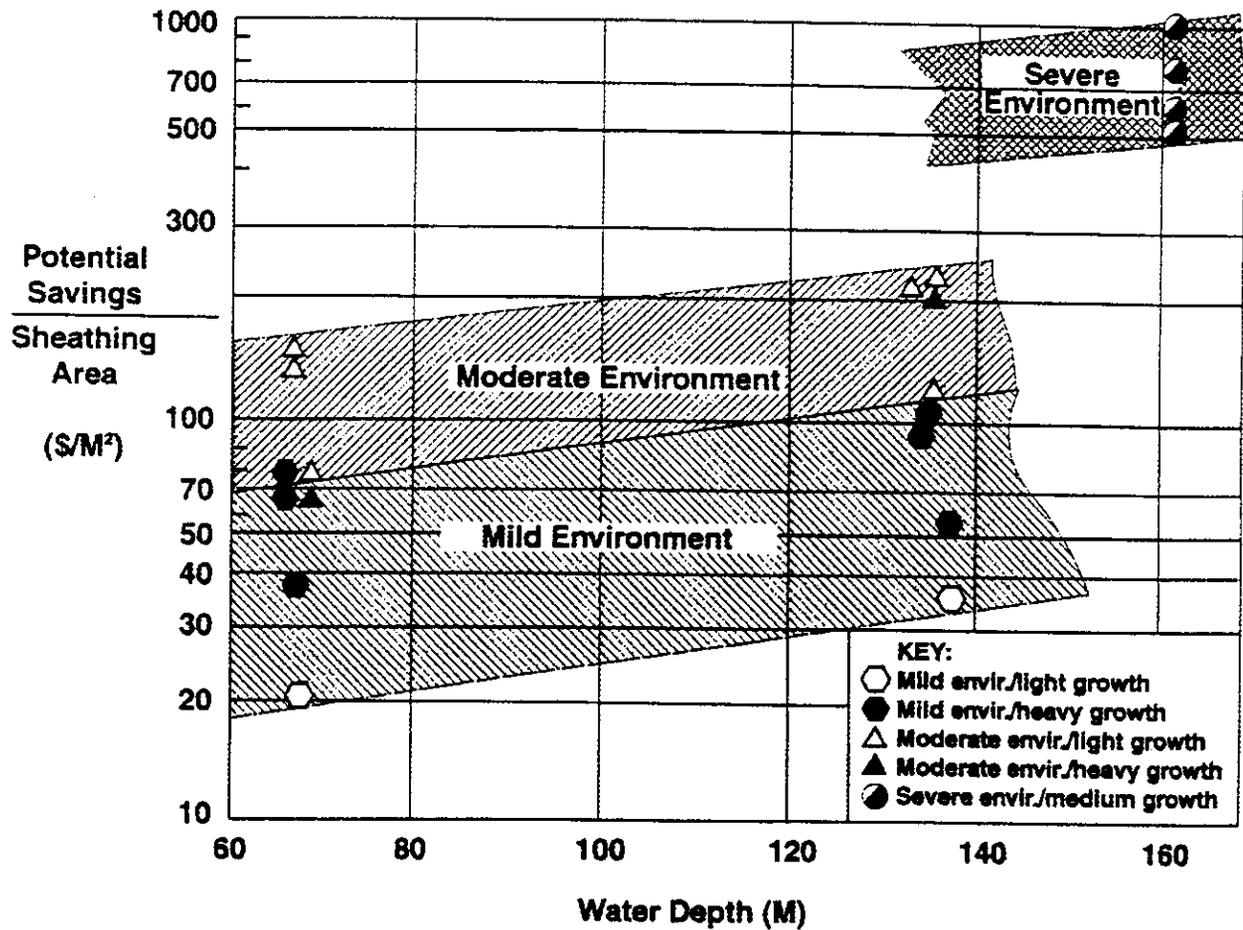
Figure 6   Potential Savings per Unit Area of Sheathing for Various Environments and Water Depths

In the mild environment, total weight savings, which is mostly attributable to reduction in steel, ranged from 9 tonnes up to 174 tonnes. For the various cases (depending on the depth of the water and the size and geometry of the off-shore structures), cost savings are up to a maximum of 5% of the total structure cost. In the moderate environment, weight savings ranged from 80 to 404 tons of steel and cost savings of 1.8% to 5.9% of total cost. The corresponding values for the severe environment were weight savings of 732 to 2372 tons of steel and 2.9% to 9.3% in cost savings.

Additional savings from reduced cleaning, maintenance and repair costs, again not included in the Exxon study, can be anticipated.

Field Experience - Sheathing Systems

British Gas Experience, Morecambe Bay, UK. The structures deployed in Stage One of the Morecambe Field project were sheathed with 90-10 copper-nickel alloy by welding 4 mm thick plate directly to the steel legs over the tidal and splash zones from 2 m below low tide level to 13 m above. A production platform, an accommodation platform, three drill platforms and a flare stack have been so treated. The main purpose of the sheathing was to provide corrosion protection in the splash zone. The submerged portion of the structure was protected by zinc anodes, which were directly attached to the steel. An economic assessment[24] indicated that the 90-10 copper-nickel alloy sheathing was more cost effective than either the 70-30 nickel-copper (Alloy 400) sheathing or conventional systems using non-metallic coatings, which necessitate increasing the thickness of the steel because of the mandated corrosion allowance for structures.

The certifying authorities required a sacrificial steel corrosion allowance (12 mm thickness) in this highly corrosive area when a paint system or neoprene wrap is specified. A sacrificial steel corrosion allowance is not required with the copper-nickel or nickel-copper (Alloy 400) metal wrap system. The economic justification was based on a platform life of 15 years. All maintenance costs were discounted to net present value at 10%. The costs associated with the painted, neoprene, and alloy sheathing approaches to protection against corrosion are summarized in Table VII

TABLE VII

ANALYSIS OF SYSTEM COSTS FOR SEVERAL COATINGS
OR SHEATHINGS FOR SPLASH ZONE PROTECTION
System Costs, Million Pounds Sterling

	Protective Coating/Sheathing			
	Paint	Neoprene	Alloy 400	90-10 Cu-Ni
Initial Cost - Extra Steel	2.3	2.3	-	-
Protective Material & Labor	0.1	0.3	2.2	0.95
Maintenance Cost	2.4[1]	unknown[2]	0.15[3]	0.15[3]
Extra Weight (tonnes)	660	660	180	180

[1] Repainting 8 years after installation and every 5 years thereafter

[2] No long-time experience; no large scale repairs assumed in less than 18 years

[3] Minimum maintenance, confined mainly to accident repair

and shown, on a relative cost basis, in Figure 7.
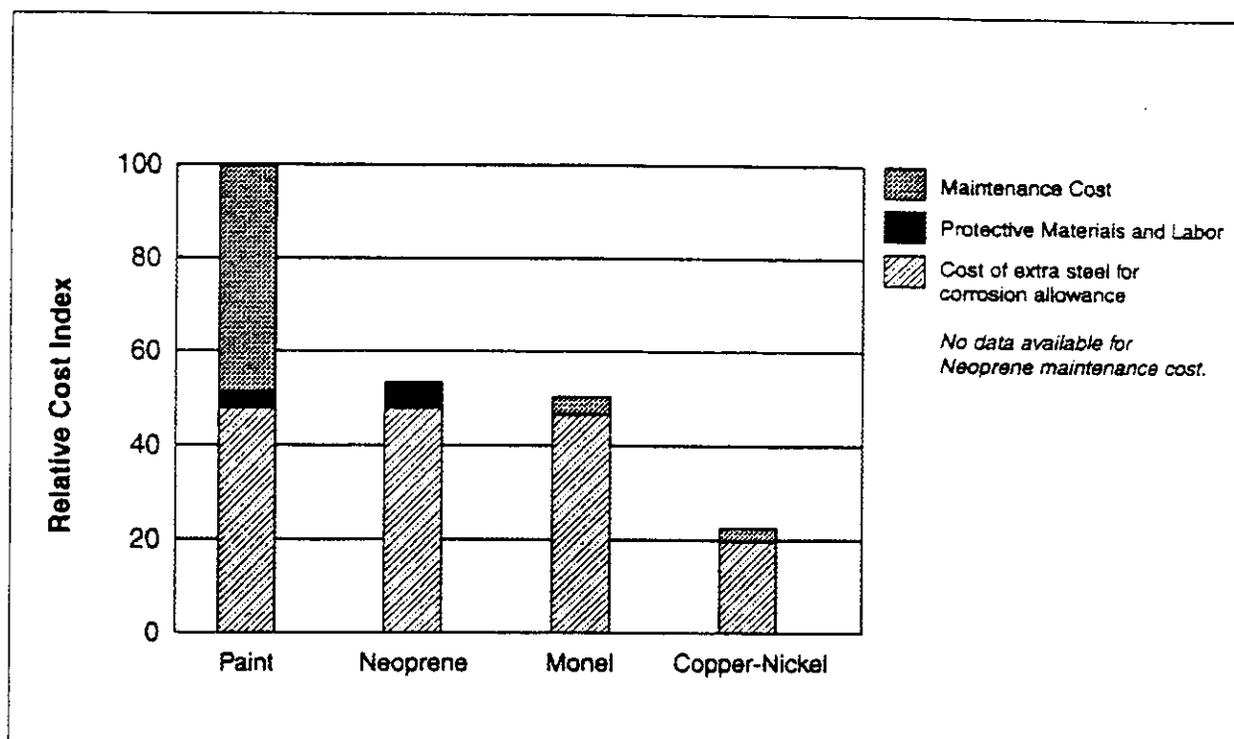
Figure 7   Relative System Costs for Protective Sheathing

The advantages of 70-30 nickel-copper (Alloy 400), and even to a greater extent, copper-nickel sheathing are apparent. For life spans in excess of 15 years, the costs savings and advantages of using the metallic sheathing systems, especially the highly fouling resistant 90-10 copper-nickel, will be even greater.

The Morecambe Field jackets have been inspected at intervals since initiation of service in 1985. Underwater video records of the condition of the steel and sheathed splash zone regions are available. These show that there is no significant corrosion of the steel or copper-nickel sheath. As a precautionary measure, the amount of cathodic protection applied was increased significantly by applying some 500 zinc anodes. With the heavy cathodic protection, there is some marine fouling on the copper-nickel since it is welded directly to the steel, but this fouling is very light compared to the steel below the sheath where heavy mussel fouling and soft hydroid growth ranging from 40 to 90 mm thick is seen.

Shell Beta Site - California. A proprietary system called "Bio-Shield" developed by the Shell Development Company, has met with considerable success on offshore installations off the coast of California[25]. Biofouling can be quite severe along the southern California coastline with three-year marine growth exceeding 200 mm immediately above to about 12 m below mean sea level. To ensure optimum effectiveness of the copper-nickel, an insulated system was selected. Bio-Shield consists of 1.6-mm thick 90-10 copper-nickel sheet and a high-density 12.5 mm thick elastomer, with the trade name of Splashtron made by the Mark Tool Company of Lafayette, Louisiana. After a laboratory test program, this system was applied to the design of the 214-m water depth Eureka platform with 60 well conductors (0.6 m OD). A total of 152 tonnes of

structural steel, otherwise required to handle the extra wave, tide and current loading from the marine growth, was eliminated. The platform was installed in July 1984. After several years, the copper-nickel surface of the Bio-Shield was free of fouling while the unprotected areas were covered with an 8 to 13 cm thick layer of barnacle and mussel growth. This attests to the effectiveness of a fully electrically insulated copper-nickel sheath. Platform response values were reduced as follows: wave forces, -6%; base shear -10%; overturning moment, -10%; deck deflection, -10%; and pile load, -7%. A reduction in platform response values directly translates into cost benefits. Reducing marine growth can clearly reduce platform costs. Money was saved in reduced steel for corrosion allowance and lower fatigue loads in the major platform joints (structural nodes). Estimated savings realized from installing the sheathing system on the 60 conductors from 1.5 m above mean low water line to 4.9 m below mean low tide for the 214 m structure are presented in Table VIII.

TABLE VIII

ESTIMATES OF COST SAVINGS FOR OFFSHORE INSTALLATIONS BY USING A 90-10 COPPER-NICKEL INSULATED SHEATHING SYSTEM

Conductors - 55 tons x $1000/ton	=	$ 55,000
Paint - 10,600 ft.² x $3/ft²	=	32,000
Anodes - $1250 each x 4	=	5,000
Structural Nodes - 114 tons x $2500/ton	=	285,000
Total	=	$377,000

Savings per cleaning were also estimated at $50,000 to $100,000. Installed costs for this system on the Eureka platform were reported to be $250,000 or about $340/m² ($31.60/ft²). Clearly, this installation of a copper-nickel sheath system was very cost effective.

Service Experience of 70-30 Nickel-Copper (Alloy 400). Field experience for 70-30 nickel-copper (Alloy 400) splash zone protection of legs dates back 50 years and for 30 years for risers.

In 1949, 70-30 nickel-copper (Alloy 400) was first used in the Gulf of Mexico, three miles from the Louisiana coast. Three materials, 70-30 nickel-copper (Alloy 400), 70-30 nickel-copper (Alloy 400) clad on steel and unalloyed nickel (Nickel 200) 1.5 mm welded sheathing were examined. All survived after more than five years of battering by boats. In conclusion, all were satisfactory but 70-30 nickel-copper (Alloy 400) was considered the most economic choice. The 90-10 copper-nickel alloy had not been fully defined at the time of this work and was not included.

Aramco first used 70-30 nickel-copper (Alloy 400) in the Arabian Gulf for legs and risers in the late 1950s, as reported by Hopkins.[26]

BP experienced splash zone corrosion in 1967 in the Middle East. Prior to that, risers were coated with coal tar epoxy, then clad with concrete. A concrete coating on a riser was damaged in Umm Shaif field due to a boat collision and the coal tar peeled off under gravity. In six months the riser wall was corroded through. Oil escaped and ignited burning down the entire

platform. BP then put 70-30 nickel-copper (Alloy 400) sheathing on 49 risers in the Gulf at 3 mm thickness. BP continued this practice when they began operations in the Forties Field in the North Sea in 1974. This has continued to the present day although neoprene is also now being used.

Phillips started to use 70-30 nickel-copper (Alloy 400) on risers following an explosion on 2-4 Alpha platform in Ekofish in 1975. Again a concrete coated riser 10 in dia. was damaged but the underlying bitumen was still intact. Severe crevice corrosion occurred and corroded 7 mm of the 10 mm thick wall in two months at 90C. The riser carrying gas fractured resulting in a massive escape of oil and gas. Phillips took action to remove all the remaining risers, and sheathed them with 5 mm thick 70-30 nickel-copper (Alloy 400) over a 25-m height span.

In 1979, at salty Lake Maracaibo in Venezuela, a riser externally coated with neoprene rubber failed due to poor application and embrittlement after four years service at 100C. A spiral defect allowed the water to reach the surface, resulting in crevice corrosion and 7 mm in corrosion penetration, which subsequently led to an explosion. Again 70-30 nickel-copper (Alloy 400) was introduced for temperatures greater than 70C.

The feedback about the performance of 70-30 nickel-copper (Alloy 400) in splash zone applications over the last 50 years has been excellent. Corrosion rates are minimal, the alloy is found to withstand sizeable impacts and tearing and the initially anticipated galvanic problems have not been realized in practice.

The authors are only aware of one type of problem area occurring in the North Sea since the 1970s. From 1987 to 1990, four failures occurred in BP 20 in risers on Forties field. A cofferdam was put around the risers to facilitate removal. The divers noted a pressure release when they removed the sheathing and hydrogen gas was detected. Destructive testing failed to find any evidence of hydrogen embrittlement. Failure had occurred at the over-stressed fillet weld at the longitudinal seam due to the pressure build-up of hydrogen between the riser and the sheathing. The pressure was 2000 to 3000 kilopascals (KPa). Wave action also introduced a fatigue element. The hydrogen was produced by internal corrosion of the riser due to poor inhibition of the wet oil. Hydrogen diffused through the riser causing a pressure buildup, and it was at such a high level that it caused mechanical damage of the sheathing. Holes were drilled in the top of the sheathing to relieve the pressure in the interim and measures were taken to ensure adequate inhibition in the longer term.

Several projects in S.E. Asia have recently selected 70-30 nickel-copper (Alloy 400) metallurgically clad pipe for hot risers as shown in Table IX.

TABLE IX

S.E. ASIA PROJECTS UTILIZING 70-30 NICKEL-COPPER (ALLOY 400)
CLAD PIPE FOR HOT RISERS

Company	Project	Materials	Diameter	Thickness	Length	Tonnage
Sarawak Shell Burhad	MLNG DUA II	API X52 plus Alloy 400 cladding	998mm	35.75 mm	70 m	60
Sarawak Shell Burhad	Bardegg	API X60 plus ASTM B127 UNS N04400	10 in	9.6 + 3 mm	18.3 m	11
			12 in	9.6 + 3 mm	18.3 m	
			18.5 in	9.6 + 3 mm	18.3 m	
Esso Production Malaysia Inc.	Gud and Lawit JEA07 and TAP 35 projects	API X65 plus ASTM B127 UNS N04400		9.6 +4 mm	15.8 m	6
				12.7+ 4 mm	13.9 m	
Esso Production Malaysia Inc.	Lawit A	API X65 plus ASTM B127 UNS N04400	30 in.	28 + 4 mm	14.3 m	9
Esso Production Malaysia Inc.	Seligi D to C	API X65 plus ASTM B127 UNS N04400	6 in.	9.6 + 4 mm	16 m	2
Sarawak Shell Burhad	Kinabalu	API X60 plus ASTM B127 UNS N04400	8 in	9.5 + 2 mm	12.2 m	7
			12 in	9.5 + 2 mm	12.2 m	
			14 in	9.5 + 2 mm	12.2 m	
Esso Production Malaysia Inc.	Tapis	API X65 plus ASTM B127 UNS N04400	24 in	22.2+ 2.5 mm	12 m	5

Limited Field Experience with 18-8 Chromium-Nickel Type 304 Stainless Steel. In 1958, two pilings were sheathed with a six-foot band of 18-8 stainless steel, which extended from above the splash zone to below the tidal zone, and driven into the mud at the wharf at the LaQue Center, Wrightsville Beach, North Carolina, USA. On one piling, the sheathing was welded at the top and bottom as well as at the overlap seam to exclude air and seawater. On the second piling, the sheathing was attached with stainless steel machine screws, but neither the top nor bottom was welded to the piling. Kirk[14] reported that the sheathing was in good shape on both pilings after 28 years of exposure, as did Kain[27] after 34 years. It is known that sacrificial zinc anodes, which were attached to the steel below the sheathing provided some cathodic protection through the mid-1980s, when this practice was discontinued. After 40 years[28] the bare steel exposed below the mud-line was near its original condition and the raised features of the welds were clearly seen. Furthermore, the steel beneath the sheathing was fully protected in both the splash and spray, and tidal zones. One thorough-wall penetration of the steel piling below the lower end of the weld sheath, which is below the waterline, was observed. In addition, local corrosion ranging or penetrations from 3.6 to 2.5 mm in depth were seen on both pilings.

The extent to which these penetrations were attributed to either self-corrosion or galvanic attack could not be determined. Stainless steel offers no biofouling resistance. The use of stainless steel should be limited to ambient temperature to avoid stress corrosion cracking. Therefore it is not an appropriate material for sheathing hot risers. However, the combination of stainless sheathing on steel pilings can be used when sacrificial zinc anodes are provided and fouling is not deemed a large issue.

Other Sheathing & Coating Systems

Zinc Clad Hydraulic Tubing. As an alternative to deep water oil platforms is to set the wellhead on the seabed and control their operation remotely with hydraulic lines. Southwestern Pipe of Houston, Texas, in cooperation with Shell Oil explored the possibility of using carbon steel wrapped in a zinc cladding to protect these hydraulic lines. A product, commercialized under the trademark SeaCAT, which consists of a 750-micron thick co-extruded zinc cladding on steel, was specified by Shell for two development projects in the Gulf of Mexico.

Thermal-Sprayed Copper-Nickel. A study conducted by Perkins and Marsh[29] at Lockheed in California demonstrated that it is technically feasible to arc-spray offshore structures with either copper or 90-10 copper-nickel. The process can be used to sheath complex shapes including nodes and welds that cannot be sheathed readily with sheet material. Free standing forms of either copper or 90-10 copper-nickel that replicate a contoured surface can also be arc-sprayed. Both arc-sprayed copper and 90-10 copper-nickel exhibited parabolic corrosion kinetics in seawater and both showed good resistance to biofouling during a 413-day exposure in San Diego harbor. These initial results show promise but additional experience is needed. Most importantly, the arc-sprayed coating allow non-destructive inspection of the underlying steel for fatigue cracks.

Adhesive Bonded Copper-Nickel. An adhesively bonded copper-nickel system known by the trade name *MITCHELL MARINER 706* has been used extensively in the sheathing of pleasure boats[30]. Wood, GRP and steel hulls have been so treated. There is no experience to date with this system on offshore structures, but it should be equally applicable there. *MITCHELL MARINER 706* consists of a 90-10 copper-nickel (C70600) foil, 0.15 to 0.25 mm in thick, where the thickness used depends upon on the intended application. The foil is coated on one side with a thick (~0.4 mm) mastic protected with a strippable backing paper. Thicker mastic layers are used for special purposes such as applying to old and pitted steel substrate after cleaning. This mastic has high electrical resistivity and very effectively insulates the copper-nickel from the steel ship hull or jacket member. It also allows some movement between the sheath and the steel and accommodates differences in thermal expansion characteristics. The mastic-coated foil is applied to the steel or other substrate with heat and some pressure. Gulf Ferries Ltd. of Auckland, New Zealand, sheathed two small ferries, both with GRP hulls, in this system in 1994.

Copper-Nickel/Resin Composite Systems

An antifouling undersea marker or identification system for pipelines, known as SEAMARK, is another interesting application of biofouling resistance of copper-nickel.[31] The markers achieve antifouling resistance from a surface layer of fine interwoven 90-10 copper-nickel wire mesh imbedded in a yellow pigmented polyester gel. The copper-nickel mesh is

insulated from the steel substrate by an appropriate backing of fiberglass, polyurethane or rubber. The markers can be adhesively bonded, vulcanized, strapped, bolted or clipped in place. The mesh is typically 0.375-mm diameter wire and is flattened and embedded in the gel. To expose the copper-nickel to the seawater, the outer surface of the composite is abraded. A minimum of 22% surface cover is required for the copper-nickel to provide adequate antifouling properties. In 1993, more than 2000 of these types of markers were sold, mostly in the Norwegian sector of the North Sea.

Another approach to providing biofouling resistance[32,33] uses 1 mm lengths of up to 1 mm diameter chopped copper-nickel wire, which is embedded in neoprene. This product, Avonclad, has now been used for more than a decade. It consists of a mono-layer of copper-nickel chopped wire embedded in and bonded to a 3 mm neoprene sheet. The chopped wire is uniformly distributed over the surface to give a copper-nickel exposure area in excess of 30%. This composite can then be either hot bonded onto an elastomeric corrosion coating or cold bonded directly onto the steel piling.

Finally, a new coating system comprised of a copper-nickel alloy applied by thermal spray to a high solid epoxy coating has been developed for antifouling application. The process, known as COPPERLOK, is applicable to fiberglass, concrete, wood and steel[34]. In the case of steel surface, the bond coat provides the necessary dielectric insulation. Good adhesion of the thermally sprayed copper is achieved by implanted hollow microspheres in the resin bond coat. These are fractured to create anchor sites for the 90-10 copper-nickel alloy.

Summary
The properties of the copper-nickel and nickel-copper alloys are reviewed. The 90-10 copper-nickel alloy is shown to have the optimum combination of corrosion and biofouling resistance. Sheathing of ship hulls with 90-10 copper-nickel is briefly reviewed, leading to the application of sheathing for corrosion and biofouling protection of offshore structures in the spray/splash zone. Trials of sheathed pilings and various attachment methods are reviewed. Sheathing of offshore structures results in reduced side forces due to tides, wind and waves. It is discussed how this translates into reductions in steel thickness and thus total jacket weight. Examples of the successful use of copper-nickel sheathing on offshore platforms and the 70-30 nickel-copper (Alloy 400) on risers are presented. Finally, several alternative sheathing systems including adhesively -bonded copper-nickel sheet and particulate copper or copper-nickel in resin matrixes are briefly introduced.

References

1. M.S. Parvizi, A. Aladjem and J.E. Castle, "Behavior of 90-10 Cupronickel in Sea Water," International Material Reviews, 33 4 (1988) pp 164-199

2. "Copper Nickel Alloys - Properties and Applications." Joint Publication of the Copper Development Association (UK) and the Nickel Development Institute, TN 30.

3. K.P. Efird and D. Anderson, "Seawater Corrosion of 90-10 and 70-30 Copper Nickel Alloys - 14 Year Exposure," Materials Performance, (141) (1975).

4. W.W. Kirk, T.S. Lee and R.O. Lewis, "Corrosion and Marine Fouling Characteristics of Copper Nickel -Alloys." CDA Conference Copper in Marine Environments, Paper 16, April 1985.

5. A.H. Tuthill, "Guidelines for the Use of Copper Alloys in Seawater," Materials Performance, 26 9 (1987) pp 12-22.

6. P.T. Gilbert, "Corrosion Resisting Properties of 90/10 Copper-Nickel-Iron Alloys with Particular Reference to Offshore Oil and Gas Applications," British Corrosion Journal, 14 1 (1979) pp 20-25.

7. J.L. Manzolillo, E.W. Thiele and A.H. Tuthill, Trans. Soc. Naval Architects and Marine Engineers Journal, 84 (1976).

8. E. Schorsch, R.T. Bicicchi and J.W. Fu, "Hull Experiments on 24-Knot RO/RO Vessels Directed Toward Fuel-Saving Applications of Copper-Nickel," Trans. SNAME 86 (1978).

9. "Copper-Nickel Sheathing Study - Phase II, Two Year Servivce Performance of Test Panels on the Arco Texas," U.S. Dept. of Transportation Maritime Administration, Contract MA-81-SAC-10074, May 1984.

10. W. Kirk, "Evaluation of Critical Seawater Hydrodynamic Effects of Erosion Corrison of CuNi," INCRA Report 396, 1987.

11. P. Drodten and H. Pircher, "Behavior of CuNi10Fe1Mn-Clad Ship Plates in Seawater," Werkstoffe und Korrosion, 41 (1990) pp 59-64.

12. E.V. Creamer, "Splash Zone Protection of Marine Structures," Offshore Technology Conference, Paper No. 1274, Houston, Texas, 1970.

13. B.B. Moreton, "Report on the Protection of Offshore Steel Structures by a Metallurgical Method," 9th Annual Conference Petroleum Division ASME," New York, N.Y., September 1954.

14. W.W. Kirk, "Metallic Sheathing for Protection of Steel in Seawater," Materials Performance, 26 9 (1987) pp 23-28.

15. R.W. Ross, Jr. and D.B. Anderson, "Protection of Steel Piling in Marine Splash and Spray Zones, - The Metallic Sheathing Concept," Proceedings of the Fourth International Congress on Marine Corrosion and Fouling, Antibes, France, June 1976, pp 461-473.

16. H. Arup, "Cathodic Current Demand of Copper-Nickel Sheathed Piling," Danish Corrosion Centre, INCRA Project No. 371.

17. J.A. Ellor & G.A. Gehring, Jr., "Galvanic Corrosion of Copper-Nickel Sheathed Steel Piling," Ocean City Research Corp., INCRA Project No. 368. March 1987.

18. S. Husa, "Stray Current Corrosion", Marintec, INCRA Project No. 372, September 1986.

19. C.J. Gaffoglio, "Concepts in Corrosion and Biofouling Control Using Copper-Nickel," Proceedings of the First OMAE Specialty Symposium on Offshore and Arctic Frontiers, New Orleans, Louisiana, Feb. 23-27, 1986.

20. D.G. Melton, "Review of Five-Year Exposure Data for CuNi-Sheathed Steel Pilings," Proceedings of the 23rd Annual Offshore Technology Conference, Houston, Texas, May 1991, pp 221-233.

21. S.J. Pikul and B.S. Phull, Thirteen Year Results of Long-Term Copper-Nickel Sheathed Piling Studies, Annual Report, ICA Project No. 358, June 1998

22. S.J. Pikul and B.S. Phull, Splash Zinc Corrosion of C70600 After Ten Years Exposure in an Oceanfront Environment, Annual Report, ICA Project No. 399, June, 1998

23. W.R. Barger, L.D. Downer, J.E. Brown and T.R. Gaul, "Economic Evaluation - Use of Copper-Nickel Alloy for Sheathing of Offshore Structures," Exxon Production Research Company, INCRA Project No. 359, September 1984, pp 21-41

24. R. Carruthers, "The Use of 90/10 Copper-Nickel Alloy as a Splash Zone Cladding," Paper 6, Proceedings of CDA Conference on Copper-Alloys in Marine Environments, (Birmingham, England) April 1985.)

25. R.F. Engel & J.P. Ray, "Bio-Shield: An Anti-fouling System for Offshore Platforms that Works!," Proceedings of Ocean Engineering and the Environment Conference, San Diego, California, United States, Vol. 1, 1985, p. 62.

26. D.J. Hopkins, "MONEL Alloy 400 Sheathing for Complete Splash Zone Protection," Offshore Europe 77, Aberdeen, September 1977.

27. R.M. Kain, "Performance and Fundamentals of Engineering Alloys in Seawater and the Marine Atmosphere," Presented at Innovations Marine Materials and Technologies Conference, La Spezia, Italy; October 1-3, 1992.

28. R.M. Kain, "Stainless Steel Sheathing for Splash and Spray Zone Protection of Steel Pilings, A 40-Year Case History," prepared for the Nickel Development Institute, June 8, 1998.

29. R.A. Perkins and D.L. Marsh, "Thermal-Sprayed Copper-Nickel Coatings on Steel," Final Report on INCRA Project 376, August 1990.

30. Canadian Yachting, August 1986, p. 18.

31. K.E.J. Miller, "Copper-Nickel Composites for Long-Term Anti-Fouling: A Review of Recent Applications," Proceedings of the Conference on Marine Engineering with Copper-Nickel, p. 95 (London, England: The Institute of Metals, 1988).

32. J.W. Brockbank, "Avonclad-a flexible neoprene/copper-nickel material for long term Antifouling; a review of manufacturing, tests and recent installations,"proceedings of Marine Engineering with copper-nickel, London, Published Institute of Materials, April 1988.

33. "Preventing Biofouling with Copper Alloys," CDA Publication 113

34. Welding Journal, April 1988, p.63.
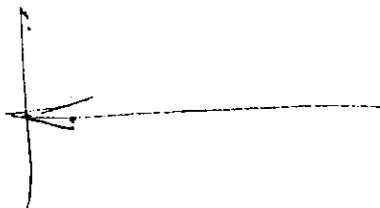
Coatings: Organic

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Organic coatings (paints) for marine applications are used primarily for protection and secondarily for appearance. The coatings are generally associated with corrosion-related degradation and failure. The coatings failures (degradation and disbondment) are a set of complex mechanisms resulting from a variety of environmental influences which affect different coatings systems in diverse ways. Degradation is cosmetically undesirable and but more importantly leads to functional failure of the intended application. Adhesion loss is not solely (simply) physical or chemical destruction of bonding between the substrate and coating. Environmental factors affecting degradation processes are reviewed including cofactors and cyclic influences. Coating tests including durability assessments are discussed with methodology for selection of appropriate evaluations. The intent of this paper is to describe a generic coatings system and the degradation mechanisms including their effects on coatings systems and to address paint durability testing in the context of marine applications including long-term deterioration modeling.

BACKGROUND

Protective coatings systems have evolved from relatively simple systems for steel consisting of phosphate/organic coatings to wide variety of complex systems consisting of metal or alloy layers, highly specialized phosphating processes, hot-applied or fused coatings, electrodeposited primers and multiple topcoats. Numerous systems are under development to determine the best possible means for meeting requirements of manufacturing, environment protection and performance. The main motivations for seeking better systems are to increase performance and durability consistent with environmental considerations and safety. This paper focuses on; 1) mechanisms of coatings degradation useful in appraising protective coatings systems when considered in the context of making overall selections for structure or facility specifications; and 2) coatings appraisals for durability.

Materials systems—An example of a coated metal system is cold rolled steel (CRS), with or without a metallic, galvanic coating such as zinc, possibly a phosphate treatment layer, an organic primer (electrophoretic primer is more frequently used for shop-produced, moderately-sized articles), spray-applied intermediate coats and an additional topcoats which can provide

considerable thickness when required. The steel substrate is protected by a system consisting of applied layers of metallic, inorganic, and organic coatings. The system provides barrier protection as well as galvanic protection in systems having active metallic phases. Figure 1 is a schematic of a representative coating system including a metallic zinc (galvanic) layer.
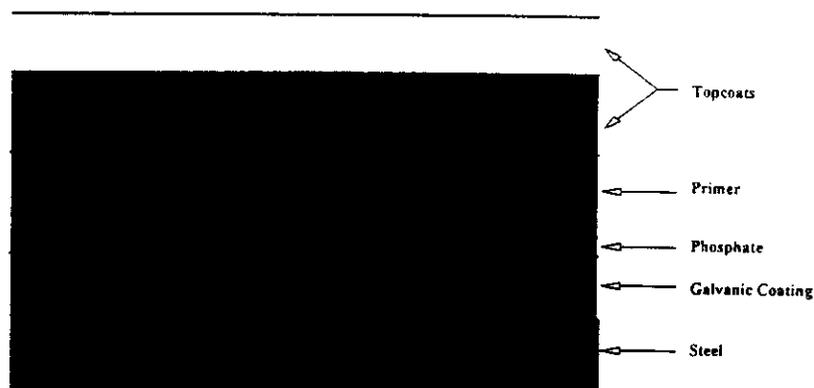
Figure 1. Coating system with multiple component layers.

Transient environmental factors—In addition to crude oil products, by-products and processing chemicals, numerous environmental factors, such as water (aqueous and vapor phases), salts, sunlight, temperature, sulfur/nitrogen oxides and acidic atmospheric components, can cause degradation and influence disbondment of organic coatings and can cause degradation and disbondment of coatings. These factors are usually very slow acting because the barrier properties of the protective system are normally adequate. Figure 2 shows the effects of chemical species transport through protective barrier coatings. However, when environmental factors are acting in concert with the presence of physical damage, the environmental factors enable rapid attack of the protective system. The cyclic nature of some factors provides a strong aggravating influence on coatings disbondment. Some of these factors are listed in Table I.

TABLE I: Environmental Factors Affecting Degradation

Factor	Effect
Ultra-violet radiation	Polymer system degradation
Water or high humidity	Polymer plasticization, corrosion
Salts	Corrosion, electrochemical processes
Sulfur/nitrogen oxides	Polymer oxidation, corrosion product
Temperature	Polymer system, corrosion reactions
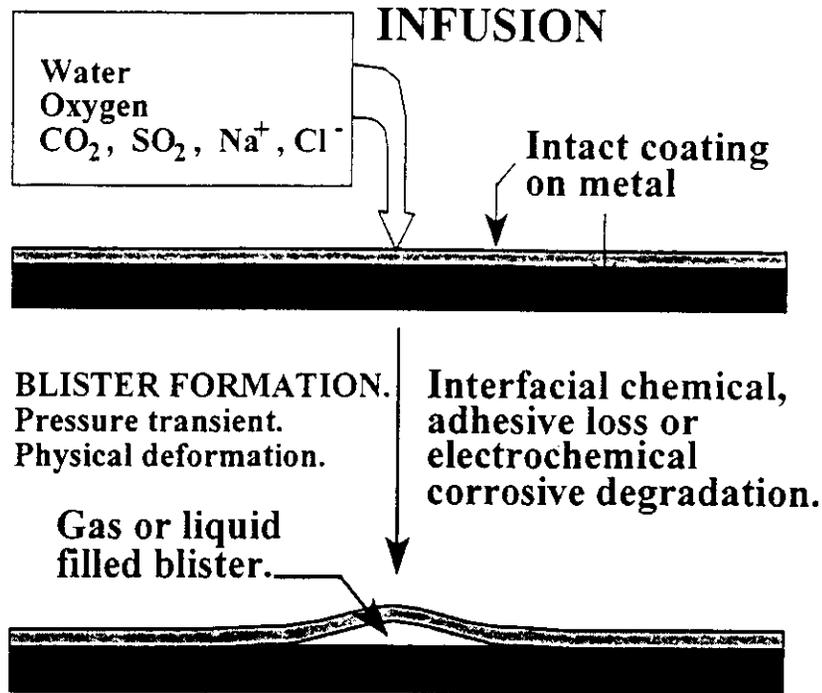
Figure 2. Infusion of degradative species and blister formation.

Crude oil products, by-products and processing chemicals have similar degradative effects, at possibly higher rates, but limited to specific working surfaces.

Two primary mechanisms of coatings disbondment are presented including their interrelationship: (1) *cathodic delamination* and (2) *mechanical delamination* associated with creep-back. An auxiliary problem is wet adhesion, which is generally reversible, although in concert with a stress may result in irreversible disbondment. Other processes which contribute to the disbondment process include anodic undermining, thermal cycling, cathodic blistering, swelling of the polymer, gas blistering and osmotic blistering. These processes are described briefly below:

Anodic undermining is the dissolution of the metal beneath the phosphate layer and is associated with the presence of cathodic regions formed at defects where the oxygen concentration level is higher or the metal coating becomes galvanically coupled to the more noble steel substrate. This process is associated with acidification resulting from hydrolysis of metal ions formed in the anodic reaction, for example,

$$Zn^{++} + H_2O = ZnO + 2H^+.$$
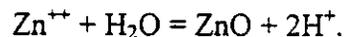
Thermal cycling, alone or in conjunction with other disbondment processes, causes stresses on the coating which can break adhesive bonds to the substrate.

Cathodic blistering is the formation of blisters associated with the electrochemical reduction of oxygen forming alkali beneath a coating having no physical damage (defect). Oxygen, water and cations diffuse through the paint film as cathodic reactants (see following Cathodic Delamination) and the center of the blister is considered the anode. The blister is usually liquid-filled due to alkali formation or may contain some gas in the cases of very low pH and very active metals.

Swelling of the polymer in some paint films is due to uptake of water which induces stress on the coating leading to possible disbondment in systems with poor adhesion.

Gas blistering is unusual, but technically possible (especially with pure Zn coatings), and is due to hydrogen ion reduction to form H_2. It is associated with acidic environments where hydrogen ion reduction is more likely than oxygen reduction.

Osmotic blistering is a process by which blistering occurs due to high water pressure induced by soluble materials beneath polymer films.

Cathodic Delamination is the mechanism by which cathodic processes cause disbondment leading to separation of a coating from a metallic substrate. The main feature of the mechanism is the reduction of oxygen at the coating/substrate interface, seen as $2H_2O + O_2 + 4e^- = 4OH^-$. This electrochemical reaction identifies oxygen, water and electrons as the required reactants. Oxygen and water are capable of diffusion through polymer coatings, although the rates vary widely with polymer type, coatings formulation and film thickness. Nonetheless, transport of oxygen and water usually occur at sufficient rates to support the reaction. Possible exceptions will be discussed later. The electrons are provided by the metal substrate conductively from anodic sites. Another prerequisite for this cathodic reaction is availability of cations for charge balance (electroneutrality). The degree to which the electrochemical reaction causes damage to the coating/metal interface depends upon the nature of cations present at or transported to the interface. The greatest damage occurs with alkali metal cations such as sodium or potassium. Alkali cations allow the attainment of the highest alkalinity (pH) at the coating metal interface. Values greater than pH = 14 have been measured. High alkalinity is greatly damaging to many polymers useful for coatings purposes; it dissolves oxides, phosphates and many types of surface treatment layers; and promotes the corrosion of metals such as iron and zinc by shifting the electrode potential to more active values. A schematic of the general cathodic delamination process is shown in Figure 3. The rate and specific mechanism for the cathodic delamination process depend on the nature of the substrate metal, interphase layers, polymer and fillers, and coating thickness, morphology and uniformity.

pH at delamination point is
determined by:

- Buffering reactions.
- Rates of diffusion of reactants to site
- Rates of diffusion of hydroxyl from site
- Volume of liquid.
- Rate of oxygen reduction.

High pH develops at this point because of reaction.

$O_2 + 2 H_2O + 4 e^- = 4 OH^-$

O_2

Metal Cation

or

Defect

Paint

Oxide or
Phosphate
Covered
Metal
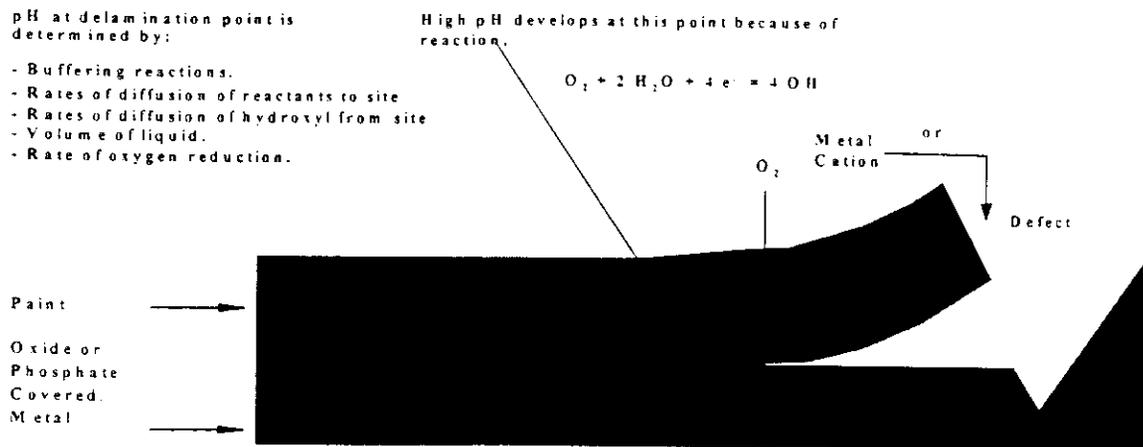
Figure 3. Cathodic delamination.

Cathodic delamination is a generally applicable mechanism for many types of polymer/metal systems such as ships, pipelines, bridges, appliances, food container liners, circuit boards and electronic components. Specific details for coatings disbondment depend upon materials, thickness and coatings system design. There are two circumstances which should be considered for cathodic delamination contributions to the disbondment process: Defect-free coatings and physically damaged coatings. In the former case, reactants for degradation process diffuse through the coating very slowly establishing what is often the rate-controlling mechanism. Thus, premature coatings system failure is not likely for systems having adequate barrier properties or low interfacial reaction rates for oxygen reduction. This statement presumes other coatings properties are adequate, such as hardness, flexibility and toughness, and that processes such as osmotic blistering due to contaminants are controlled by proper attention to material and application quality. In the latter case, reactants are transported to the reaction sites through the physical defects. Accordingly, degradation can occur rapidly, dependent upon the aggressiveness of the environmental factors and the ability of the coatings system to resist the corrosive attack associated with the physical defect. A subset of this latter case occurs when the physical damage does not completely perforate the polymer coating system. In the case of partial perforation, the result can be cathodic blister formation with little or no rust formation until the blister cracks or breaks.

Mechanical Delamination—In the context of this paper, mechanical delamination is the disbondment of the paint film from the substrate caused by corrosion product formation. The main significance of this delamination mechanism is in its relationship to corrosion processes generating stresses resulting in the propagation of coating system damage.

The origin of stresses causing mechanical delamination at scribes and blisters is associated with the anodic corrosion reaction generation of metal cations (Fe^{++} or Zn^{++}) and their precipitation. In the case of zinc ions, precipitation is mainly due to achieving a sufficiently high zinc ion concentration by anodic process, water evaporation, pH effect or combination with anions. In the case of iron ions, the precipitation is due to the same effects as for zinc, plus oxidation of ferrous to ferric ion by oxygen, which causes precipitiation of the less soluble ferric

compounds. Precipitates for zinc and iron include oxides, hydroxides, oxychlorides and sulfates. Solid phase corrosion products are known to exert high stresses in crevice geometries and easily lift delaminated paint films. The lifting of the paint film forms a cavity near the advancing delamination front which can serve as a reservoir for water, alkali cations (sodium) and oxygen.

Combined Effects —Cathodic delamination at the paint film/phosphate-metal interface, anodic undermining at the delamination front (loci of chemical attack) and mechanical delamination associated with volumous corrosion product precipitation from the area of original paint film damage provide the means for a catalytic effect on the overall disbondment mechanism under cyclic environmental conditions. The mechanism has a catalytic component in the sense that upon completion of each wet/dry cycle, the process proceeds at an increased rate due to reactant resupply at the delamination front.

Physical damage —The most direct cause for initiation of coatings disbondment is physical damage due to chipping, scratches, scrapes and dents. Some of these processes are accidental in nature and are avoidable. However, the most widespread damage is caused by mechanical impact on wear or contact surfaces or by wave action in the splash zone. Some accelerated corrosion tests attempt to mimic this effect. Physical damage of the protective system enables more rapid transport of aggressive materials (water, salts, gases and other contaminants) from the environment to the metallic phases where disbondment and corrosive degradation processes occur. Figure 4 shows a schematic of a damaged coatings system. Thus, the barrier properties of the protective system are impaired or destroyed and, disbondment and corrosive degradation proceed more rapidly at, and adjacent to the damaged sites. Figure 5 shows modes of degradation associated with specific layers or interfaces of the coating system.

PAINT SYSTEMS AND CORROSION

Protective polymeric coatings fall broadly into three different classes: lacquers, varnishes and paints. Varnish is a term applied to coatings which are solutions of either a resin alone (hardens with exposure to air or moisture) in a solvent (spirit varnishes) or combinations of an oil and a resin in a solvent (oleoresinous varnishes). The term lacquer is generally limited to a composition whose basic film former is nitrocellulose, cellulose acetate-butyrate, ethyl cellulose, acrylic resin or other resin that dries by solvent evaporation. The term paint is applied to more complex formulations of a liquid mixture that dry or harden to form a more degradation-resistant protective coating. Typical formulation constituents include a liquid vehicle which may be water or an organic solvent, pigments to give the coating color, fillers to maintain coating thickness at low cost, wetting agents to promote penetration of the paint into scratches and pores in the substrate, anti-foaming agents, anti-mildew agents, catalysts to cause polymerization of some coatings, corrosion inhibitors, and constituents which control the rheological properties. Other constituents may also be included in order to obtain a special property in the coating.
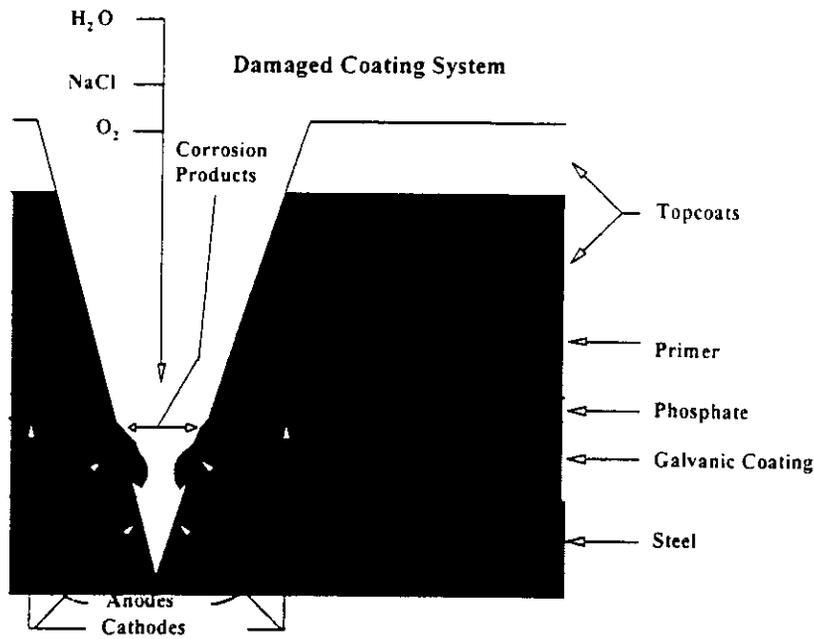
Figure 4. Schematic of damaged coating system.
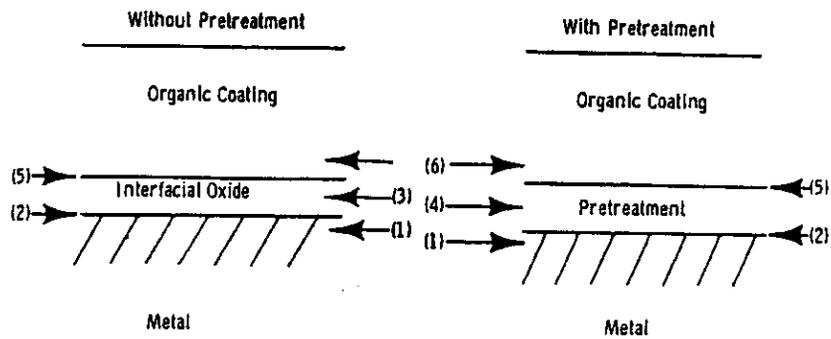
Figure 5. Degradation of associated with specific layers or interfaces of the coating system.

A polymeric coating protects a metal substrate from corroding by two mechanisms: (1) serving as a barrier for the reactants, water, oxygen and ions; and (2) service as a reservoir for corrosion inhibitors that assist the surface in resisting attack. Coatings which contain large quantities of dispersed, metallic zinc also provide corrosion protection by galvanic action. The barrier properties of the coating are improved by increased thickness, by the presence of pigments and fillers that increase the diffusion path for water and oxygen, and by the ability to resist degradation. The common degradation mechanisms of the coating include abrasion and impact, cracking or crazing at low or high temperature, bond breakage within the polymer matrix because of hydrolysis reactions, oxidation, ultraviolet light, and freeze-thaw cycling. The result

of such degradation allows access of reactants to the coating/substrate interface without the necessity of diffusion through the polymer matrix.

Corrosion of a metal beneath a polymeric coating is an electrochemical process that follows the same principles as corrosion of an uncoated metal. What makes the process different from crevice corrosion, for example, is the fact that the reactants often reach the metal through a solid (paint). Also the small volumes of liquid that are involved in the early stages of corrosion result in extreme values of pH and ion concentrations. The total corrosion process may be thought of in terms of the following components:

- Transport properties of the coating for water, oxygen and ions

- Development of an aqueous phase at the coating/metal interface

- Activity of the metal surface for anodic and cathodic reactions

- Deterioration of the coating/metal interfacial bond

These component processes are accelerated by physical damage to the coatings system.

COATINGS SYSTEM

The coatings system is comprised of several component layers which interact with adjacent layers and, occasionally, separated layers. The following are summary descriptions for the system components:

Substrate—The substrate is the foundation for the coatings system. It is usually steel, but may be steel coated with a galvanic material such as zinc or a zinc alloy, or it may be aluminum or a composite material. It any case the substrate may be inert, reactive or it may simply be soiled or in need of cleaning and pretreatment. A significant effort has been devoted to development of appropriate specifications for preparing substrates for receiving protective and decorative coatings. For preparation of large areas of steel, abrasive blasting is commonly used. Standards have been developed characterizing the degree of blast treatments and the materials used for these purposes [2].

Conversion coatings—The most common conversion treatment for steel and galvanically coated steel substrates is phosphating. Application of these coatings is usually restricted to fabrication shop facilities on components amenable to wet spray treatments. The process involves many steps and includes removal of soils, preservatives, oxides, deposition of a phosphate crystallite layer (usually a zinc phosphate modified with nickel) and the optional application of a sealing treatment (chromate or non-chromate). Conversion coatings provide corrosion protection and an excellent adhesion interface for organic coatings, especially electrocoat.

Electrocoating—The primer coat can be an electrocoating in which the part is immersed in an aqueous, suspension of paint and electric current applied to plate or deposit the organic layer. The uncured deposit has the physical stability of a gel which is then rinsed and baked to

cure the paint. The electrocoat provides the major portion of the corrosion protection to the part. As in the case of conversion coatings, electrocoating is usually restricted to shop application facilities.

Primers—These coatings are the first coat with the purpose of providing good adhesion between the substrate and subsequent coats. A wash primer is a thin coating which provides corrosion inhibitive properties. Most primers contain anticorrosive materials usually in the form of pigments or fillers.

Topcoats—Color coats are applied over the primer coat to complete the protective coatings system. These coatings provide protection from ultraviolet (UV) light which could degrade epoxy-based intermediate or midcoats. Also, topcoats provide protection from impact damage. Materials designed to easily develop substantial protective thickness are referred to as high-build coatings.

Additional details on surface preparation, type and use of specific coatings, application methods and suggested specifications are available from a variety of sources [2-5].

OBSERVATIONS OF COATINGS SYSTEMS FAILURES

Coatings system failures may be due to several causes such as physical damage, chemical degradation or latent defects. Physical and chemical causes are of primary importance, whereas latent causes, including improper surface preparation and coatings application methods related to quality control or material selection, will be largely disregarded in the context of this discussion. The usual observations of damage associated with coatings degradation are related to scratching, chipping, gloss-loss, chalking and rust staining. These observations are objectionable from aesthetic considerations in addition to being precursors for more serious degradation and systems failures such as general rusting, perforation, creep-back and delamination. The modes of degradation associated with chemical changes in the polymer system are usually sufficiently slow to be acceptable when considered alone. The most serious degradation problems are related to physical damage which permits acceleration of chemical degradation processes. In recognition of this modality, most accelerated test procedures include scribing or chipping in combination with environmental exposures. These procedures are not intended solely to decrease the time required for testing, but represent realistic forms of in-service damage which the coating system must tolerate. The disbondment of various coatings systems has many similar elements except with regard to the color of the corrosion products, white with metallic zinc coatings and red without zinc, and the rate of disbondment. Also, in the absence of galvanically protective coatings, creep-back (flaking/underfilm corrosion from defect) is more obvious and perforation by pitting is more likely.

DURABILITY TESTS

Available Tests and Standards

Existing tests and standards are under continuous development. New tests are being designed. ASTM is a leader of tests and standards; other contributors, with various emphasis on specifications, are the federal government with Federal Test Method Standard 141C, state

government agencies, NACE International. Society of Automotive Engineers (SAE), National Coil Coaters Association (NCCA), International Standards Organization (ISO), foreign systems (DIN), commercial (e.g. automotive, architectural, electronics), proprietary and military. A comprehensive listing of these tests and standards is not the intent of this document. The American Bureau of Shipping (ABS) offers useful guides for protective coatings.

Gaynes [6] and Munger [7] give descriptions and the framework for effective use of tests and standards. Gaynes [6] provides detailed descriptions including photographs, cross-listing ASTM to federal tests and a broader perspective encompassing the federal standards, miscellaneous tests, and some caveats of traditional testing. Munger [7] offers practical material directed towards large structures and provides a listing based upon ASTM standards. Altmayer [8] compiled a table of 13 applicable corrosion tests for 30 metallic, inorganic and organic coating/substrate combinations. The most commonly used tests are salt spray (ASTM B 117), acetic acid salt spray (ASTM G 85, Annex A1—formerly ASTM B 287) and the 100% humidity (ASTM D 2247). A condensed listing with brief descriptions of tests selected from Altmayer [8], Mazia [9], ASM International [10] and others is given in Appendix Table I. Additional tests are listed in Appendix Table II, an edited and revised listing by Munger [7]. Hess [13] provides a very important auxiliary reference aiding in identifying the causes of paint film defects.

Methods Selection

The large number of tests and methods makes selection potentially bewildering. Suppliers, users, testers, and researchers have different perspectives to help narrow the selection process. Obtaining corrosion resistance information enables a better focus. To aid in the selection process where no universal methodology exists, engage one or more from a: (1) survey of practices; (2) specific practice by a successful coatings industry participant; (3) coatings service life testing philosophy; and/or (4) useful practical example involving cooperative efforts through better understanding (methodology).

Survey of Practices—A survey commissioned by the Federation of Societies for Coatings Technology (FSCT) was performed by the Steel Structures Painting Council (SSPC) [12]. The full report [13] is available from FSCT and contains useful details including non-standard tests and analyses. One portion of the report is particularly relevant to methods selections; a compilation of 102 coatings test users' responses is shown in Table II, from which two conclusions are drawn: (1) Most respondents used only 1 or 2 tests; (2) The most prevalent test was salt spray. Salt spray testing is a crude approximation to highway environments involving deicing compounds [13] (see also fourth account below, "Cooperative...") and more useful for marine systems [13]. Coatings users may approach quality assurance with fewer tests than formulators [13]. A considerate case describing salt spray test usefulness or uselessness based upon years of experience is presented by Liu [14].

TABLE II—Survey Results of 102 Responses: Frequently Used Tests

Test	% Respondents*
Salt spray	52
Immersion	24
Outdoor	22
Ultraviolet/condensation	20
Accelerated weathering	14
Humidity/condensation	10
Cathodic disbondment	7
Adhesion	7
Atlas cell test (NACE TM0174)	4
Other physical tests	4
Other chemical tests	3
Flexibility	2

* Multiple tests used (total greater than 100%)

A Specific Practice—The following tests constitute a generic test plan used by one industrial service company for coated metal in laboratory performance testing. A 4"×12" coated panel is the preferred configuration. Before accelerated corrosion tests (ASTM B 117, G 85-A1, B 368 and G 85-A3), a scribe is introduced using ASTM D 3359-Method-A or D 1654-Section-5. Exposure times are 240-1000 h, depending on the test and substrate. Additional corrosion tests (unscribed and ASTM D 714 evaluation) include hot humidity (ASTM D 2247, 100°F/100%RH), condensing humidity (ASTM D 4585, 140°F), condensing humidity/UV (ASTM G 53, 150°F), water soak (ASTM D 870), and detergent soak (ASTM D 2248, 72 h). Scribed samples are prepared for ASTM D 1654 evaluation by scrape/rinse/dry, rinse/blow-off or 3M's #610 tape pull-off. Other non-corrosion tests (mainly adhesion) are also performed including T-Bend, Wedge Bend, Conical Mandrel, Impact (Direct/Reverse), MEK rub (cure test), Olsen Cup, Gravelometer, Pencil Hardness, Cross-Hatch, Dry Film Thickness, and Loss of Gloss. This battery of tests provides generous information about the coatings system, without establishing a direct link to service data. The test battery is necessarily extensive because the intent is to determine possible causes for service problems. A clear relationship between service and test data is necessary for problem resolution.

Service Life Testing Methodology—In the above example of "A Specific Practice," no rationale is given for the selection or application of the tests. Experience provides an important gauge for developing a useful set of tests. Dickie [15] suggested that a methodology be developed to provide rational guidance for service life testing, and proposed a general framework integrating laboratory experiments, field exposure history, and theoretical and empirical models. The central role of physical and chemical models of degradation processes in service life prediction was examined [15] and represents an important philosophical contribution for coatings testing. The methodology was first presented in a somewhat different form at an informal meeting of experts discussing coatings failure mechanisms [16].

Cooperative Practice Yielding Better Understanding—AISI [17,18] has taken a leadership role to develop and evaluate methodology based upon laboratory experiments, field exposure history, and theoretical and empirical models through an open forum of all interested parties (mainly North American automotive and steel industries), organized as the Corrosion Task Force of the AISI. The Task Force's goal is to develop an improved laboratory accelerated test for ranking the cosmetic corrosion resistance of automotive steel sheet products where "many years of field experience have shown just the opposite" [17] results (compared to ASTM B 117 for this application). The Corrosion Task Force has implemented their work as an SAE procedure (J-2334) which is described as a schematic in Figure 6. This approach taken by the Corrosion Task Force serves as a model for methodology development in areas of nonmetallic coatings corrosion testing.

EXAMPLES OF COATINGS SYSTEM

Figures 7-8 are examples of coatings systems for discussion purposes. Generic descriptions are given in the figure captions.

RESEARCH METHODS

Figures 9-12 give examples of research methods, EIS and PALS, used for protective coatings research and development [19,20].

AUTHOR'S NOTE

This paper is provided for educational purposes and is a synthesis of topics mainly from two articles [1,21]. The articles should be consulted for additional details.
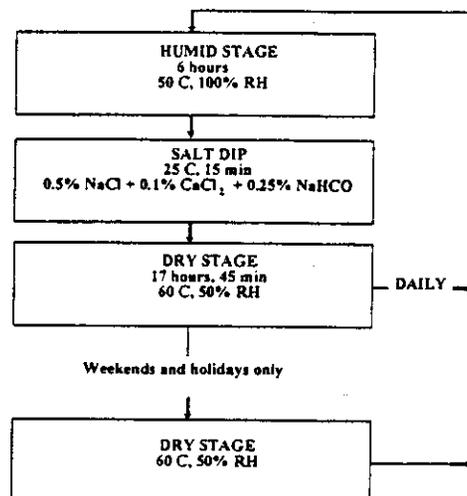
Figure 6. Schematic of SAE Method J-2334.
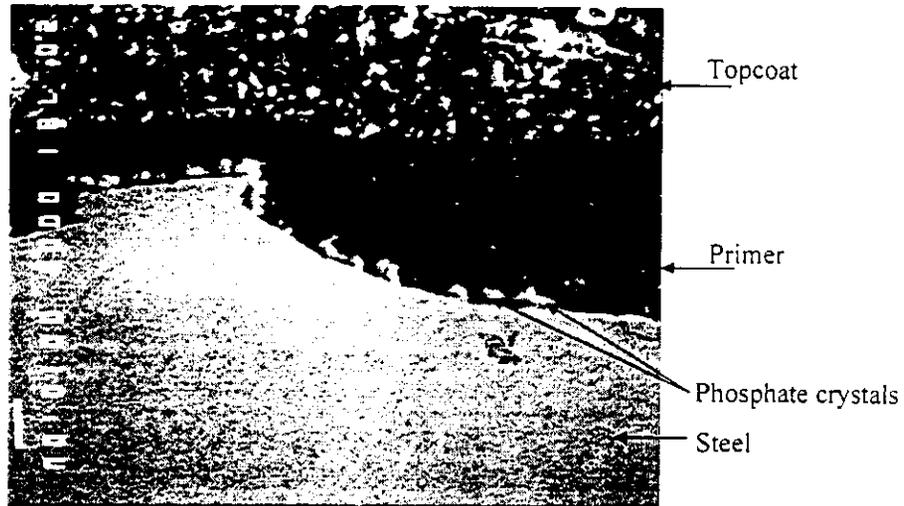
Figure 7. Coating system example 1. Cross-section of pretreatment beneath coating system.

Local thinning can provide notch for fatigue crack

Figure 8. Coating system example 2. Section thinning at drainage detail.

Impedance Spectrometer
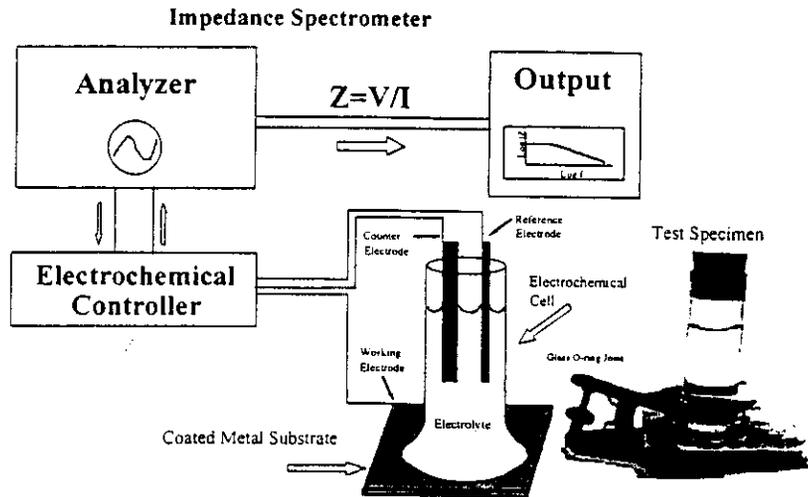
Figure 9. Schematic of impedance measurement system and test specimen.

Cathodic polarization curves of NiAlBronze in NaCl at various rotational velocities.
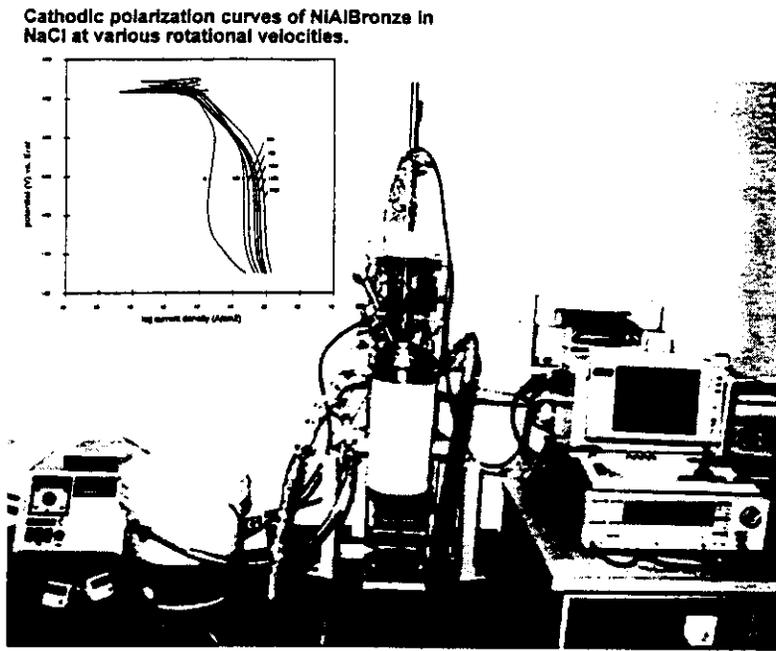
Figure 10. Photograph of impedance system for high pressure and hydrodynamic conditions including temperature and oxygen concentration control.

- Free volume is the intermolecular space between atoms, molecules, and polymer chains that accommodates thermal motion.

- Temperature, pressure, and molecular weight changes alter the free volume resulting in changes in the physical properties of polymers, e.g.

- *Increase temperature:* increase free volume, decrease Young's modulus

    - *Increase pressure:* decrease free volume, increase viscosity

    - *Increase molecular weight:* decrease free volume, increase glass transition temperature

FREE VOLUME

Unoccupied Space * Between Molecules
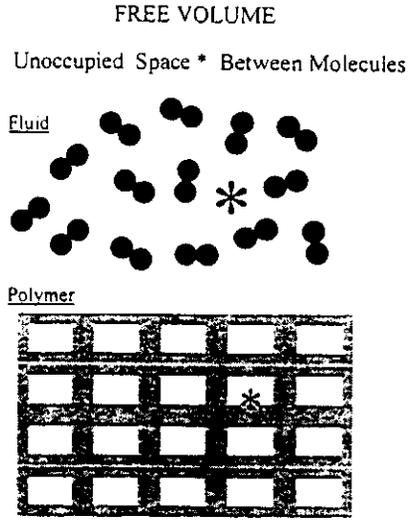
Figure 11. Free volume and polymer coating properties.
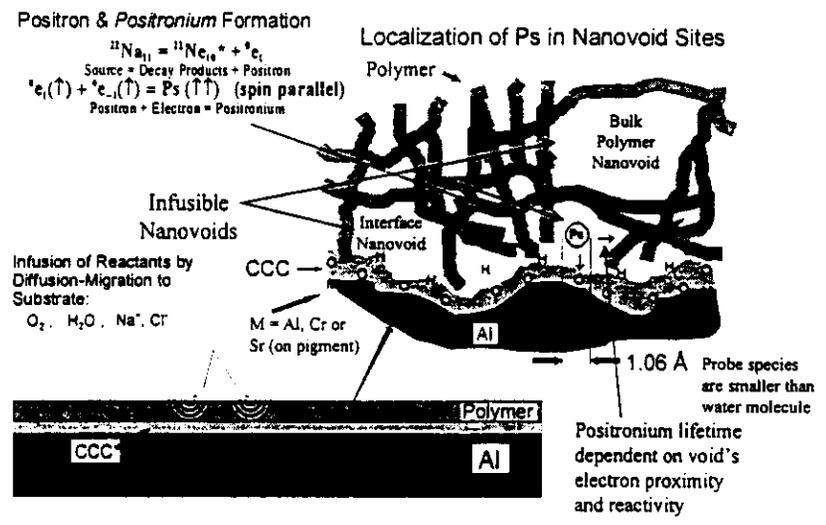
Figure 12. Schematic of PALS (positron annihilation lifetime spectroscopy) for nanovoid measurements of barrier coating properties. Positrons probe void structures involved in coatings degradation process.

REFERENCES

[1] Granata, R. D., "Mechanisms of Coatings Disbondment," Corrosion'91, NACE, Houston, TX, Paper No. 91/382.

[2] NACE Standard RP0176-94, Standard Recommended Practice, Corrosion Control of Steel Fixed Offshore Platforms Associated with Petroleum Production, NACE International, Houston, TX (1994).

[3] Metals Handbook 9th Edition, Vol. 13, Corrosion, ASM International, Metals Park, OH, pp. 398-418 (1987).

[4] Guidance Notes on Marine Coating Systems, American Bureau of Shipping (1998).

[5] Douglas Dopjera, BP Corporation, Coatings Technology Paper, April, 1999 .

[6] Gaynes, N. I., Testing of Organic Coatings, Noyes Data Corporation, Park Ridge, NJ, 1977.

[7] Munger, C. G., Corrosion Prevention by Protective Coatings, National Association of Corrosion Engineers, Houston, TX, 1984, Chapter 12.

[8] Altmayer, F., "Choosing an Accelerated Corrosion Test," Metal Finishing, 61st Guidebook and Directory Issue, Vol. 91, No. 1A, Metals and Plastics Publications, Hackensack, NJ, January, 1993, pp. 483ff.

[9] Mazia, J., "Testing Organic Coatings Systems," Metal Finishing, 59th Guidebook and Directory Issue, Vol. 89, No. 1A, Metals and Plastics Publications, Hackensack, N.J., January, 1991, pp. 590ff.

[10] (a) Sandler, M. H., "Nonmetallic Coating Processes: Painting," Metals Handbook, Vol. 5: Surface Cleaning, Finishing and Coating, 9th edition, ASM International, Metals Park, OH, 1990, pp. 489-498 and pp. 527-531; (b) Scully, J. R., "Electrochemical Methods of Corrosion Testing: Electrochemical Evaluation of Protective Coatings and Films," Metals Handbook, Vol. 13: Corrosion, 9th edition, ASM International, Metals Park, OH, 1987, pp. 219-220.

[11] Hamburg, H. R. and Morgans, W. M., eds., Hess's Paint Film Defects: Their Causes and Cure, Chapman and Hall, London, 1979.

[12] Appleman, B. R., "Survey of Accelerated Test Methods for Anticorrosive Coating Performance," Journal of Coatings Technology, Vol. 62, No. 787, August, 1990, pp. 57-67.

[13] Appleman, B. R., "Survey of Accelerated Test Methods for Anti-Corrosive Coating Performance," Monograph prepared for Corrosion Committee of Federation of Societies for Coatings Technology, June, 1990. Available from FSCT, Blue Bell, PA.

[14] Liu, T., "Is the Salt Fog Test an Effective Method to Evaluate Corrosion Resistant Coatings?" in Corrosion Control by Organic Coatings, Leidheiser, H., Jr., editor, National Association of Corrosion Engineers, Houston, TX, 1981, pp.247-54.

[15] Dickie, R. A., "Toward a Unified Strategy of Service Life Prediction," Journal of Coatings Technology, Vol. 64, No. 809, June, 1992, pp. 61-64.

[16] Funke, W., et. al "Unsolved Problems of Corrosion Protection by Organic Coatings: A Discussion," Journal of Coatings Technology, Vol. 58, No. 741, October, 1986, pp. 79-86.

[17] Townsend, H. E., "Status of a Cooperative Effort by the Automotive and Steel Industries to Develop a Standard Accelerated Corrosion Test," Automotive Corrosion & Prevention Conference Proceedings, Dearborn, MI, 1989, SAE Technical Paper Series, Paper No. 892569, pp. 145-57.

[18] Townsend, H. E., "Development of an Improved Laboratory Corrosion Test by the Automotive and Steel Industry," in Advanced Coatings Technology, Proceedings of the Fourth Annual Engineering Society of Detroit Advanced Coatings Conference, Engr. Soc. Detroit, Ann Arbor, MI, 1994, pp. 29ff.

[19] MacQueen, R.C., Miron, R.M., and Granata, R.D., "Method for Corrosion Inhibition Mechanism Studies in Epoxy Coated Aluminum," Journal of Coatings Technology, Vol. 68, No. 857, June, 1996, pp.77ff.

[20] Madani, M.M., Miron, R.M., and Granata, R.D., "PALS Free Volume Study of Dry and Water Saturated Epoxies," Journal of Coatings Technology, Vol. 69, No. 872, September, 1997, pp.45ff.

[21] Granata, R. D., "Materials Testing, Non-Metallic Coatings," in Manual on Corrosion Tests and Standards: Application and Interpretation, ASTM Manual Series, MNL 20, ASTM, Philadelphia, PA, 1995, pp. 525-530.

APPENDIX TABLE I—Brief Descriptions of Selected Tests

Test	Description and Remarks
Salt Spray, (ASTM B 117)	Most widely specified test. Atomized 5% sodium chloride, neutral pH, 35°C*, follow details of ASTM B 117, Appendix X1. Emphasizes wet surfaces (non-drying), high oxygen availability, neutral pH and warm conditions. Control or comparative specimens should be run simultaneously. Corrosivity consistency should be checked as described in ASTM B 117, Appendix X3. Notes: May be the most widely misused test. Requires correlation to service tests for useful results. Do not assume correlation exists.
100% Relative Humidity, (ASTM D 2247)	Widely used test. Condensing humidity, 100% RH, 38°C. Emphasizes sensitivity to water exposure.
Acetic Acid-Salt Spray ASTM G 85, A1 (formerly ASTM B 287)	Widely used test. Atomized 5% sodium chloride, pH 3.2 using acetic acid, 35°C. More severe than ASTM B 117. The lower pH and the presence of acetate affect the solubility of corrosion products on and under the protective coatings.
Sulfur Dioxide-Salt Spray (ASTM G 85, A4)	Atomized 5% sodium chloride, collected solution pH = 2.5-3.2, 35°C, SO_2 metered (60 min × 35 cm^3/min per m^3 cabinet volume) 4 times per day.
CASS (copper accelerated salt spray), (ASTM B 368)	Atomized 5% sodium chloride, pH 3.2 with acetic acid, 0.025% cupric chloride-dihydrate, 35°C. Galvanic coupling due to copper salt reduction to copper metal. More severe than ASTM B 117.
FACT (formerly ASTM B 538)	Testing anodized aluminum specimens. Electrolyte as in salt spray or CASS test. Specimen is made the cathode to generate high pH at defects.
Accelerated Weathering	Exposure of coated specimens to effects of UV radiation experienced in outdoor sunlight conditions which may be combined with other exposures such as moisture and erosion. Exposure cabinets use carbon arc (ASTM D-822), xenon lamp (ASTM G-26) or fluorescent lamp (ASTM G-53).
Acidified Synthetic Seawater Testing (SWAAT), ASTM G-85, A3 (formerly ASTM G-43)	Atomized synthetic seawater (ASTM D 1141) with 10 mL glacial acetic acid per liter of solution, pH 2.8 - 3.0, 35°C. More severe than ASTM B 117. The lower pH and the presence of acetate affect the solubility of corrosion products on and under the protective coatings.

* Note that dissolved CO_2 concentration at 0°C is 3 times that of concentration at 35°C and can affect corrosion.

APPENDIX TABLE I, Continued.

<u>Test</u>	<u>Description and Remarks</u>
Electrographic and Chemical Porosity Tests	Pores and active defects in nonmetallic coatings can be revealed by color indication or deposit formation. On nickel substrates, dimethylglyoxime, or steel, potassium ferricyanide (ferroxyl test), indicator can be applied to surface on filter paper while substrate is made the anode. Alternatively, a substrate immersed in acidic copper sulfate can be made the cathode to form copper nodules at conductive coatings defects.
Adhesion ASTM D 3359-90	Knife and fingernail test consists of cutting through the coating with knife or awl and dislodging coating with thumbnail or fingernail (pass/fail). The ASTM D 3359 test consists of "X" scribes or parallel cross-hatches followed by adhesive tape stripping of loosened coating.
T-Bend Adhesion ASTM D 4145	Combined flexibility and adhesion test consists of clamping end of coated flat metal panel in vise or similar tool, bending (convex) through 90°, reclamping to bend through 180° to give "0T" bend (where "T" is panel thickness and # (zero, 1, 2,...) is the number of panel thicknesses). Rebending over the 180° bend gives a "1T" bend. Adhesive tape is pressed down along edge of bend and any loose coating stripped off.
Scab Test	Cyclic testing consisting of short salt exposure, short drying period and long period of high humidity. Undercutting from scribe is measured.
Exterior Exposure ASTM D 1014	Method for conducting exterior exposure tests of paints on steel. Well-defined exposure setup—Not necessarily equivalent to service tests.
Service Test/Data	Performance data of coatings systems under use conditions. Slowest evaluation method; provides tangible results.

APPENDIX TABLE II—Coatings Tests and Methods Pertinent to Corrosion Protection[a]

NACE† or ASTM Standard	Title of Standard
†TM0174-91	Laboratory Methods for the Evaluation of Protective Coatings and Lining Materials in Immersion Service
B 117-90	Standard Test Method of Salt Spray (Fog) Testing
B 287-87[b]	Method of Acetic Acid-Salt Spray (Fog) Testing
B 368-85 (1990)[ε1]	Method for Copper Accelerated Acetic Acid-Salt Spray (Fog) Testing (CASS Test)
D 522-92	Standard Test Methods for Mandrel Bend Test of Attached Organic Coatings
D 523-89	Standard Test Method for Specular Gloss
D 610-85 (1989)[ε1]	Method for Evaluating Degree of Rusting on Painted Steel Surfaces
D 662-86[ε1]	Method for Evaluating Degree of Erosion of Exterior Paints
D 714-87	Method for Evaluating Degree of Blistering of Exterior Paints
D 822-89	Practice for Conducting Tests on Paint and Related Coatings and Materials Using Filtered Open-Flame Carbon-Arc Light and Water Exposure Apparatus
D 823-92a	Test Methods for Producing Films of Uniform Thickness of Paint, Varnish, Lacquer, and Related Products on Test Panels
D 870-92	Standard Practice for Testing Water Resistance of Coatings Using Water Immersion
D 968-81 (1991)[ε1]	Standard Test Methods for Abrasion Resistance of Organic Coatings by Falling Abrasive
D 1014-83 (1988)[ε1]	Method for Conducting Exterior Exposure Tests of Paints on Steel
D 1186-87	Method for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to a Ferrous Base
D 1400-87	Test Method for Nondestructive Measurement of Dry Film Thickness of Nonconductive Coatings Applied to a Nonferrous Metal Base
D 1653-91a	Test Method for Water Vapor Transmission of Organic Coating Films
D 1654-92	Method for Evaluation of Painted or Coated Specimens Subject to Corrosive Environments
D 1735-87	Practice for Testing Water Resistance of Organic Coatings Using Water Fog Apparatus
D 2197-86 (1991)[ε1]	Test Methods for Adhesion of Organic Coatings by Scrape Adhesion
D 2247-87	Practice for Testing Water Resistance of Coatings in 100% Relative Humidity
D 2248-89	Standard Practice for Detergent Resistance of Organic Finishes
D 2803-82 (1987)	Standard Test Method for Filiform Corrosion Resistance of Organic Coatings on Metal

[a] Revised from Munger [7], p. 318.
[b] Discontinued, see ASTM G 85 for replacement

**NACE† or
ASTM Standard**   **Title of Standard**

D 3258-80 (1987)$^{\varepsilon 1}$ ..... Test Method for Porosity of Paint Films

D 3273-86 (1991)$^{\varepsilon 1}$ ..... Standard Test Method for Resistance to Growth of Mold on the Surface of Interior Coatings in an Environmental Chamber

D 3276-86 .... Guide for Paint Inspectors (Metal Substrates)

D 3359-90 .... Test Methods for Measuring Adhesion by Tape Test

D 3361-87 .... Practice for Operating Light- and Water-Exposure Apparatus (Unfiltered Carbon-Arc Type) for Testing Paint, Varnish, Lacquer, and Related Products Using the Dew Cycle

D 3363-74 (1989)$^{\varepsilon 1}$ ..... Test for Film Hardness by the Pencil Test

D 4145-83 .... Standard Test Method for Coating Flexibility of Prepainted Sheet

D 4585-92 .... Standard Practice for Testing Water Resistance of Coatings Using Controlled Condensation

D 4587-91 .... Standard Practice for Conducting Tests on Paint and Related Coatings and Materials Using a Fluorescent UV-Condensation Light- and Water-Exposure Apparatus

E 376-89 .... Practice for Measuring Coating Thickness by Magnetic-Field or Eddy-Current (electromagnetic) Test Methods

G 53-91 .... Standard Practice for Operating Light- and Water-Exposure Apparatus (Fluorescent UV-Condensation Type) for Exposure of Nonmetallic Materials

G 60-86 .... Method for Conducting Cyclic Humidity Tests

G 80-88 .... Test Method for Specific Cathodic Disbonding of Pipeline Coatings

G 84-89 .... Practice for Measurement of Time-of-Wetness on Surfaces Exposed to Wetting Conditions as in Atmospheric Testing

G 85-84 (1990)$^{\varepsilon 1}$ .... Practice for Modified Salt Spray (Fog) Testing

G 87-84 (1990)$^{\varepsilon 1}$ .... Practice for Conducting Moist SO_2 Tests

G 90-91 .... Practice for Performing Accelerated Outdoor Weathering of Nonmetallic Materials Using Concentrated Natural Sunlight

G 92-86 (1992)............ Standard Practice for Characterization of Atmospheric Corrosion Test Sites

[a] Revised from Munger [7], p. 318.
[b] Discontinued, see ASTM G 85 for replacement

Cathodic Protection of Offshore Structures and Pipelines –Historical Development, Present Knowledge, and Future Challenges

by

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Abstract

Cathodic protection, either alone or in conjunction with coatings, is generally recognized as the most technically and economically effective corrosion control alternative for the submerged portion of marine structures, including ships, space frame petroleum production platforms, and pipelines and risers. The historical development of cathodic protection and the importance of 1) calcareous deposits, 2) rapid polarization, and 3) the newly developed slope parameter design method are reviewed. It is projected that a limitation of the current Recommended Practices that pertain to cathodic protection of fixed offshore structures is that these are empirical and that values for key parameters of the design equation, namely 1) mean current density and 2) anode current capacity, do not reflect actual service performance. Cathodic protection design is even less technically mature in the case of pipelines and risers, where the existing equations for potential attenuation and anode current output are non-conservative. Such short-fallings become of particular concern as industry continues to focus upon deep water and frontier ocean locations. Steps and directions whereby these limitations can be addressed are presented and discussed.

Introduction

General

There are six fundamental corrosion control alternatives for engineering structures, components, and systems exposed to a hostile environment, as listed below:

1. Design for corrosion control.
2. Proper materials selection.
3. Coatings.
4. Inhibitors.
5. Cathodic protection.
6. Modified operating conditions.

Generally speaking, category 1 and 2 alternatives pertain to the design stage and are implemented during construction or fabrication. A simple example is provision of additional member thickness to allow for uniform corrosion wastage. While consideration of and attention to corrosion should be inherent to any marine design and materials selection activity, this is often not the case; and reduction or loss of structure functionality in the long-term can be the consequence. On the other hand, once fitness for purpose is identified as an issue, it may become necessary to modify the operating conditions, as called for by item 6 above.

Coatings, cathodic protection, and inhibitors have been utilized for corrosion control for the better part of this century, either as part of the original design and construction or subsequently once specific corrosion problems have been identified. However, coating of submerged structures or portions thereof can normally be performed prior to deployment only; and inhibitors are an option for open sea water applications only as these might be incorporated in a coating. Alternatively, cathodic protection, either as a stand-alone corrosion control method or in conjunction with coatings, has now evolved to become the primary option for the submerged portion of steel marine structures, including ships, petroleum production platforms, and pipelines.

History of Marine Cathodic Protection

The concept of cathodic protection was first conceived and studied some 170-plus years ago, as reported by the classic papers of Davy (1-3). These studies were performed over about a two year period and included laboratory experiments, harbor exposures, and sea trials on ships. From the results, Davy developed extraordinary insight into the principles of corrosion and corrosion prevention, as exemplified by the following conclusions:

1. A requisite for corrosion of copper in sea water is presence of dissolved oxygen. Weak salt solutions attack copper more rapidly than strong ones because of greater oxygen dissolution in the former compared to the latter.

2. Corrosion rate of copper in sea water can be nulled by reducing the electrochemical state to a value more negative than the naturally occurring one.

3. A practical means of altering potential of copper to a more negative value is by coupling to a metal such as zinc, tin, or iron.

4. The protection afforded copper by contact with a more active metal is independent of the geometrical positioning of the latter upon the former and, within limits, of the size and length of the electrical lead connecting the two.

5. Corrosion activity upon copper contacted by a more active metal decreases with increasing area ratio of the latter to the former. Above a critical area ratio, which is a function of the electrolyte, corrosion rate of the "defended" metal (cathode) is nil.

2

Davy also reported the presence of "alkaline substances", now termed calcareous deposits, upon the cathode and, upon analysis, concluded that these were "... principally carbonated lime, and carbonate and hydrate of magnesia" (2). These were noted to be more pronounced the larger the anode-to-cathode area ratio and the less the water movement. There is no indication, however, that the importance of calcareous deposits in reducing the amount of required anode material or in extending the life of cathodic protection was recognized.

Despite the long history of marine cathodic protection, the techniques employed in its application still utilize, with some exceptions, tradition and overly simplified methods rather than sound scientific and engineering principles. These exceptions are based upon comprehensive studies by the U. S., Canadian, and British navies during the 1940's and 1950's (4), as reviewed recently by Peterson (5), and subsequent research and development activities manifested by the increased number of fixed offshore structures and the transition in petroleum production focus to progressively deeper water. However, despite these activities, many cathodically protected ships today operate with an impressed current system that consists of relatively few anodes and perhaps a single reference electrode. The limited experiments and analyses that have been performed indicate that the resulting hull potential can range from under- to over-protected depending upon location and operating conditions (6).

Cathodic protection was first utilized upon offshore petroleum production structures about 50 years ago. These initial systems were, in most instances, minimally engineered and were successful largely because of overdesign. However, marine cp technology has become more advanced and refined during the course of the ensuing decades; and standards and recommended practices are now available which address design and practice (7,8). Of particular importance is the criterion that is employed for projecting if the level of cathodic protection for steel in sea water is adequate. Several of these are available; however, a requirement that polarization be to at least -0.80 v (Ag/AgCl reference) has evolved as prevalent. It is generally accepted that such a potential criterion for protection correspond to polarization of cathodic sites to the reversible value for the anodic reaction; and theoretical considerations, subject to certain assumptions, have shown this to be approximately the case (9). Other developmental hallmarks include recognition of 1) the beneficial role of calcareous deposits (10-17), 2) the concept of rapid polarization (18-22), and 3) the slope parameter approach to cp design and data analysis (23-26), are discussed subsequently.

Principles of Cathodic Protection

The principles of cathodic protection are best expressed using the classical polarization diagram representation of the potential-current interrelationship for a corroding metal. Figure 1 illustrates this, where the electrode kinetics for both the anodic (iron/steel oxidation) and cathodic reactions, as comprised of both oxygen and hydrogen reduction, are shown. Corroding steel, as is represented here in terms of its potential (ϕ_{corr}) and current (I_{corr}), is cathodically polarized; that is, its potential is made more negative, by application of a positive, externally provided current, I_{appl}, through the

electrolyte which, in conjunction with the local action anodic and cathodic currents (I_a and I_c, respectively) necessarily conforms to Kirkoff's law or

$$I_c = I_a + I_{appl}. \tag{1}$$

Superimposed upon the polarization curves in Figure 1 are three levels of cathodic polarization (different values for I_{appl}) which represent partial, complete (adequate), and over-protection. Thus, at the intermediate level of polarization ($I_{appl(1)}$) potential is necessarily $\phi_{(1)}$ since this is the only value for this parameter where Equation 1 is satisfied. Relatedly, with adequate protection the potential of the metal becomes □ϕ_{Fe}, the reversible anode potential, at which the anodic current is zero. Correspondingly, at this and more negative potentials corrosion rate is nil. For this potential range ($\phi \leq \phi_H$), where ϕ_H is the reversible potential for the hydrogen reaction, oxygen is reduced everywhere according to
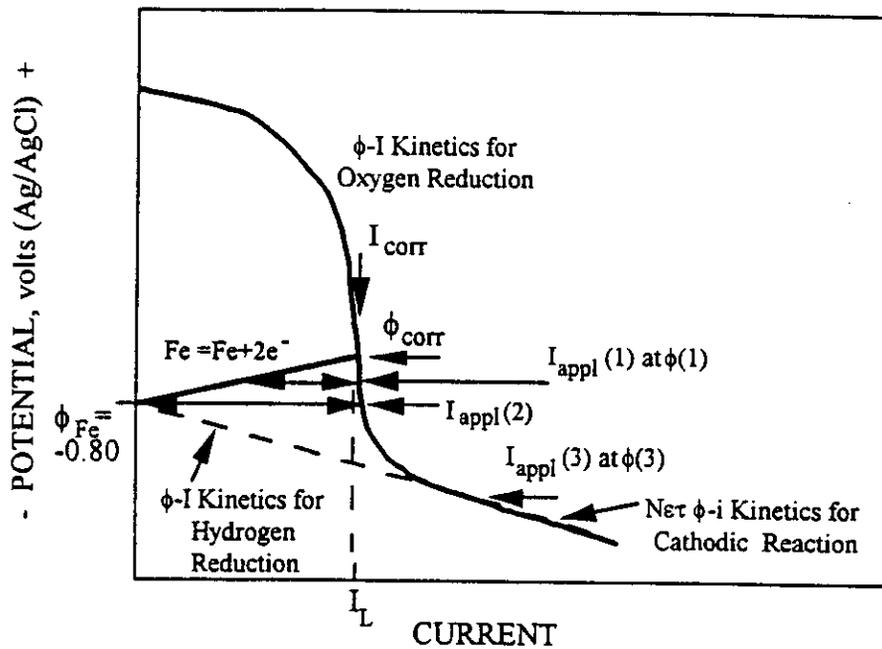
Figure 1: Polarization diagram illustrating the principle of cathodic protection.

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-, \tag{2}$$

and the entire surface is a cathode. At potentials negative to the reversible hydrogen value (shown in Figure 1 as approximately the same as ϕ_{Fe}) hydrogen reduction or

$$H_2O + 2e^- \rightarrow H_2 + OH^-, \tag{3}$$

4

also occurs, which causes the cathodic current to increase excessively for $\phi \leq -1.05$ v. Other disadvantages of over-protection include 1) the possibility of hydrogen embrittlement and 2) damage to any protective coatings that might be present. For reasons that are made clear subsequently, the target potential range for most cathodic protection systems is negative to -0.80 v by from $0.10-0.25$ v.

The applied current required to achieved a prescribed degree of cathodic protection depends upon the slope of the anodic and cathodic polarization curves with kinetics of the latter (cathodic) reaction being the more influential. Thus, Figure 1 reflects a quiescent water exposure, as indicated by the relatively steep slope to the oxygen reduction portion of the cathodic reaction curve and low limiting current (I_L). With increasing water movement or reduced tendency for surface film (calcareous deposit) formation (or both) oxygen availability and the rate of reaction 1 increase, which causes a corresponding increase in I_{corr} and I_{appl} at a given potential. Figure 2 illustrates schematically different oxygen reaction kinetics situations and how this effects I_{appl}. Consequently, an important component of cathodic protection design is definition of oxygen availability and provision accordingly for adequate applied current.
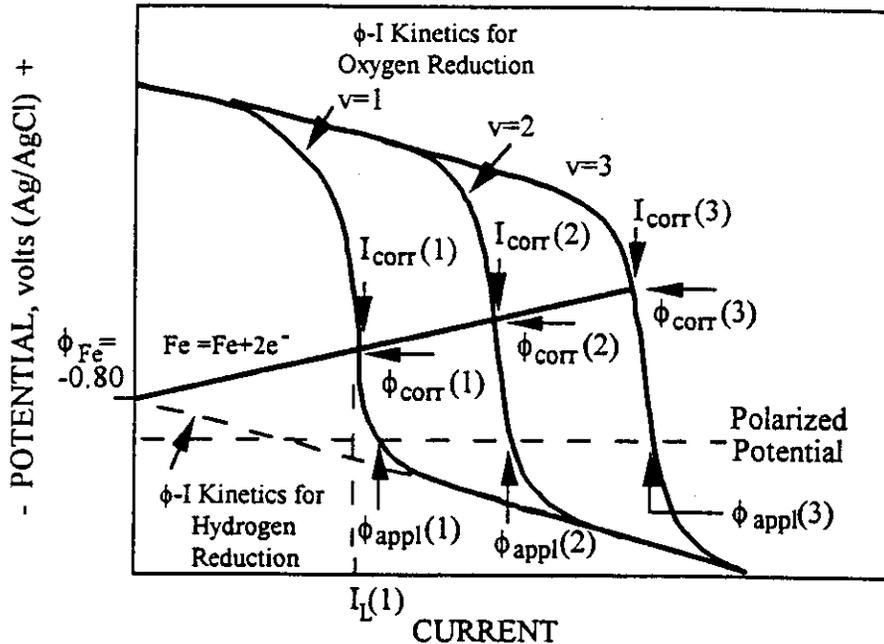
Figure 2: Polarization diagram for steel in sea water illustrating the potential and current for cathodic protection.

Types of Cathodic Protection Systems

Based upon the above discussion, the objective in design of marine cathodic protection systems is definition of the applied current to polarize the steel structure of interest to from -0.90 to -1.05 v (Ag/AgCl). This is accomplished using either an impressed or galvanic anode system, where the former is based upon a direct current rectifier and inert anode and the latter solely upon an anode whose native potential is active to that of the steel structure. Figure 3 schematically illustrates each of these.

5

Hybrid and bimetallic systems have also been employed to a limited extent, where the former combines the two basic system types (impressed and galvanic) and the latter uses two types of galvanic anodes (magnesium and aluminum, for example (27)). Advantages of galvanic systems include the following:

1. External power is not required.
2. Installation is relatively simple.
3. Reliability is high.
4. Polarization commences upon immersion.
5. Electrical leads cannot be reversed.

Disadvantages, on the other hand are:

1. Current output of the system cannot be varied.
2. The anodes often contribute to structural loading.
3. Greater expense in the case of large structures.

Generally, advantages of galvanic systems constitute disadvantages for impressed current ones and visa versa. Based upon the second disadvantage, galvanic systems alone are impractical for ships; and impressed current in conjunction with coatings is employed instead (supplemental galvanic anodes may be added in high current demand areas). On the other hand, reliability considerations (advantage one above) result in galvanic anodes being preferred for petroleum production structures; and geometrical factors and unavailability of electrical power (advantage one) dictate this same system type for marine pipelines.

Design of Marine Cathodic Protection Systems

General

Emphasis in the present discussion is placed upon galvanic anode cathodic protection systems because these predominate in the case of marine petroleum production structures and pipelines/risers. These two structure groupings, production platforms and pipelines/risers, are fundamentally different with regard to cp because the former are space frames with three dimensional anode arrays whereas the latter are linear with discrete, flush mounted anodes. Thus, while anodes on platforms can be viewed as providing protection to steel in their immediate vicinity, they also contribute to the current field overall. In the case of pipelines and risers, however, potential attenuates with distance from the anode such that an individual anode is more critical as far as protection within its domain is concerned. Consequently, pipelines and risers are invariably coated, whereas most space frame structures are not, so that current demand is reduced and protection is extended to a greater distance from the individual anodes.

The fact that maintenance of adequate protection for pipes and risers is more difficult than for space frame structures, as explained above, may account for the fact that failures have been more prevalent for these. Thus, reports and publications pertaining to

the occurrence and cause of offshore Gulf of Mexico pipeline failures indicate that there were 690 accidents of sufficient magnitude to be recorded by the MMS during the period from 1967 to 1987 (28-30). Of these, 343 (50 percent) resulted from corrosion with a total of 85 percent of these being documented as involving either external or general attack. During this same 20 year period the failure rate increased at an average of over two per year. This is thought to have been a consequence of 1) increased pipeline population and offshore construction activity with time and 2) aging of the pipeline infrastructure. Despite the significance of this particular problem (external corrosion of marine oil and gas pipelines) relatively little attention has been focused upon it as evidenced by the fact that the 1991 International Workshop on Offshore Pipeline Safety (31) included only one paper which explicitly focused upon this topic.

Cathodic Protection Design of Production Platforms

The recommended practices addressing cathodic protection design of fixed offshore structures (7,8) are based upon determination of the current output per anode, I_a, as calculated from Ohm's law according to the expression

$$I_a = \frac{\phi_c - \phi_a}{R_a},$$

(4

where

ϕ_c = closed circuit cathode potential,
ϕ_a = closed circuit anode potential, and
R_a = resistance of an individual anode.

For three dimensional or spaceframe type offshore structures, anode resistance is normally the dominant component of the total circuit resistance; and so it alone is considered. In most cases this term is calculated from standard, numerical relationships which are available in the literature (32-38) based upon anode dimensions and electrolyte resistivity. Figure 3, which is a modification of Figure 1, graphically illustrates the principle behind Equation 4. For pipelines, on the other hand, both the coating and metallic pipeline resistances may also be important.

From the net current for protection (Equation 4) the number of anodes required for protection, N, is determined from the relationship

$$N = \frac{i_c \cdot A_c}{I_a},$$

(5

where

i_c = cathode current density for polarization and
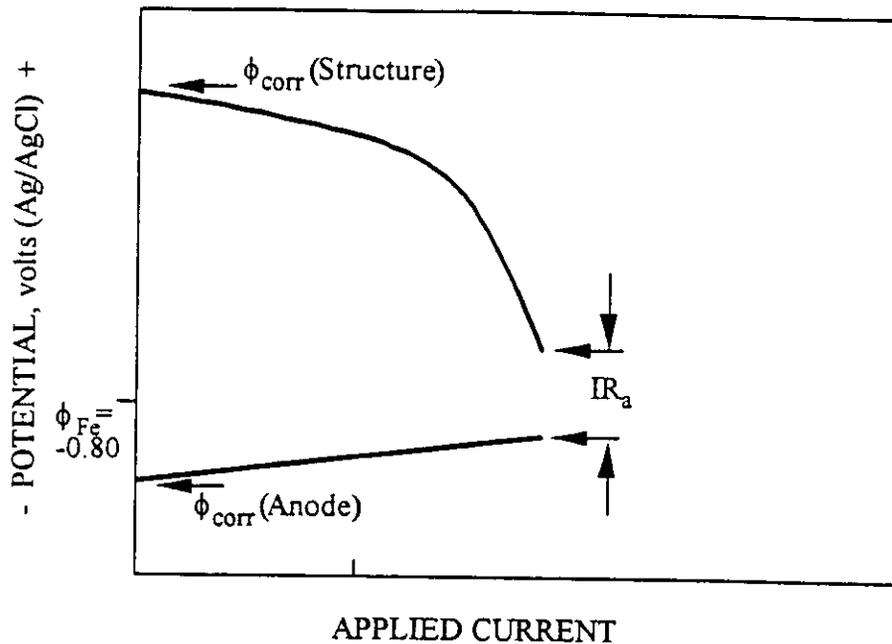
Figure 3: Schematic illustration of a polarization diagram and of parameters relevant to galvanic anode cathodic protection system design.

A_c = cathode surface area.

Calcareous Deposits and Rapid Polarization

Historically, cathodic protection design was based upon a single current density which polarized the structure to the potential required for protection; that is, to -0.80 v (Ag/AgCl), within from several months to one year (39). This relatively lengthy period for polarization was a consequence of the design current density being low such that development of surface films (calcareous deposits) and associated oxygen concentration polarization was slow. However, field surveys of structures that were designed according to this practice have often revealed potentials that were 100 to 250 mV more negative than -0.80 v; and the life of the cathodic protection system for these has often exceeded what was projected in the initial design. For example, Evans (40) reported that potential for several platforms in the Arabian Gulf was on the order of -0.94 v after 15 years, although the original design was for only ten. Most of the anodes on these structures had become depleted, but apparently the small current that continued to flow provided protection. Similarly, Cochran (41) indicated that 77 of 100 platforms protected by galvanic anodes exhibited potentials of -0.92 v or more negative. A 33 year cp system life was estimated for one platform which exhibited potentials in the range -0.91 to -0.99 v after 4.5 years, whereas the original design was for 20 years.

The above observations can be explained by the experiments of Cox (42) who, some fifty-plus years ago, demonstrated that initial application of a relatively high current density resulted in formation of calcareous deposits that were particularly protective and

which yielded a lower maintenance or long-term current density than if the initial value for this parameter was low. Based either upon laboratory or service data, several authors (18-23) have revisited during the past one-to-two decades the high initial current density concept; and this technology is now being employed routinely for cp system design of offshore petroleum production structures. Accordingly, the current recommended practices which address this technology (7,8) incorporate rapid polarization by specification of a relatively high initial current density (i_o), such that a structure potential in the range -0.90 to -1.00 v results "...within a reasonably short period of time" (7). The design also includes two other criteria, one based upon a maintenance current density (i_m) and the other upon a final current density (i_f). Values for N to satisfy the requirement imposed by i_o and i_f are determined using Equations 4 and 5, where each of these current densities replaces i_c. The criterion upon which i_f is based intends to ensure that adequate anode mass remains at the end of the design life to affect repolarization should this become necessary. The maintenance current density, on the other hand, is the long-term or steady-state value for this parameter and, as such, is equivalent to the single current density employed in the earlier protocol (39). The number of anodes required to provide this current is calculated from the relationship

$$N = \frac{i_m \cdot A_c \cdot T}{C \cdot w},$$
(6

where

T = design life,
C = anode current capacity, and
w = weight of a single anode.

Typical values for these three design current densities are listed in Table 1 (8). Ideally,

Table 1:Design current densities for different ocean locations.

Production Area	Typical Design Current Density, mA/m^2 (mA/ft^2)		
	Initial	Mean	Final
Gulf of Mexico	110 (10)	55 (5)	75 (7)
U.S. West Coast	150 (14)	90 (8)	100 (9)
Cook Inlet	430 (40)	380 (35)	380 (35)
Northern North Sea	180 (17)	90 (8)	120 (11)
Southern North Sea	150 (14)	90 (8)	100 (9)
Arabian Gulf	130 (12)	65 (6)	90 (8)
Australia	130 (12)	90 (8)	90 (8)
Brazil	180 (17)	65 (6)	90 (8)
West Africa	130 (12)	65 (6)	90 (8)
Indonesia	110 (10)	55 (5)	75 (7)

9

each of the three calculations should yield the same N; however, this is invariably not the case; and so the highest of the three is specified. For uncoated structures, this is normally the N that corresponds to the initial current density. Accordingly, the cathodic protection system may be over-designed in terms of the other two current density requirements. This failure of the design procedure to yield a common number of anodes for each of the three current density criteron arises because the procedure is simply an algorithm rather than being first principles based.

Figure 4 presents data from a series of experiments where 25 mm diameter by 51 mm high API Grade 42 steel cylinder specimens were galvanically coupled in natural sea water to an aluminum anode ring through an external resistor (R_x), the size of which varied for each test (23). By interconnecting the 24 hours exposure data points, a polarization curve, the slope of which is negative at all potentials and which is indicative of limited oxygen concentration polarization, becomes apparent. However, similar curves for progressively greater exposure times reveal progressive development of a sigmoidal trend. Figure 5, which shows the 3200 hour and additional longer-term data, illustrates in greater detail the steady-state potential-current density $(\phi\text{-}i)$ relationship that results from this type of experiment. These results and the data representation that has been employed here render apparent the basis, if not the mechanism, for rapid polarization in that the current density which ultimately results from modest cathodic polarization, such that the protection potential (-0.80 v (Ag/AgCl)) is achieved only in the long-term, was about 2.5 times greater than if the steady-state potential were near -1.00 v.
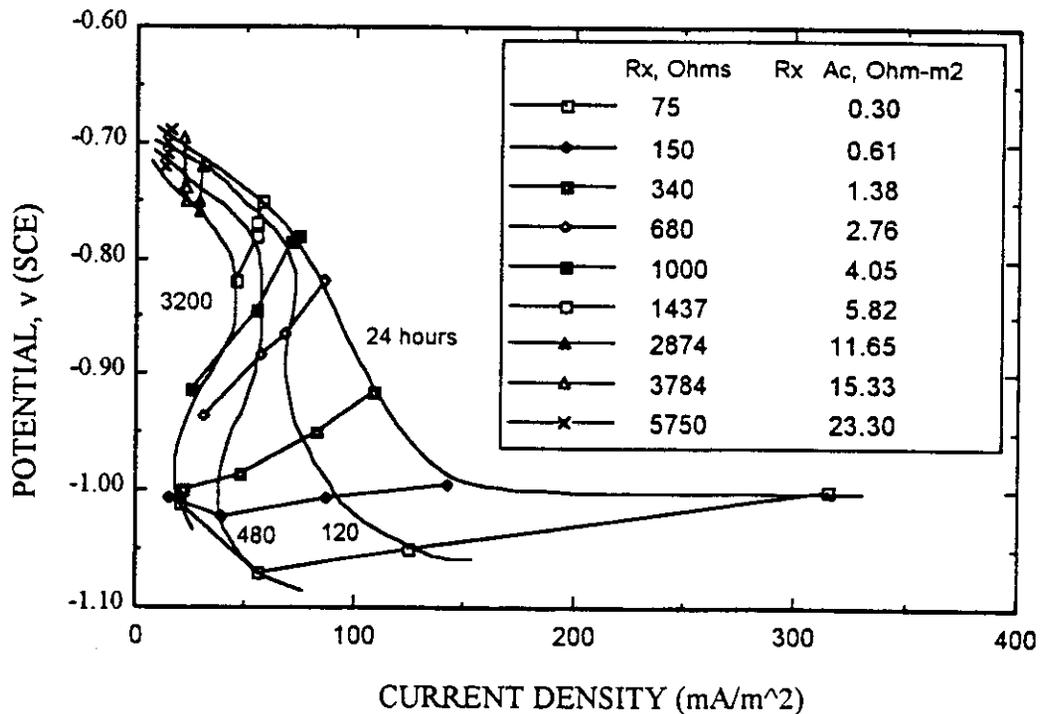
Figure 4: Cathode potential versus current density for representative laboratory experiments at different exposure times.
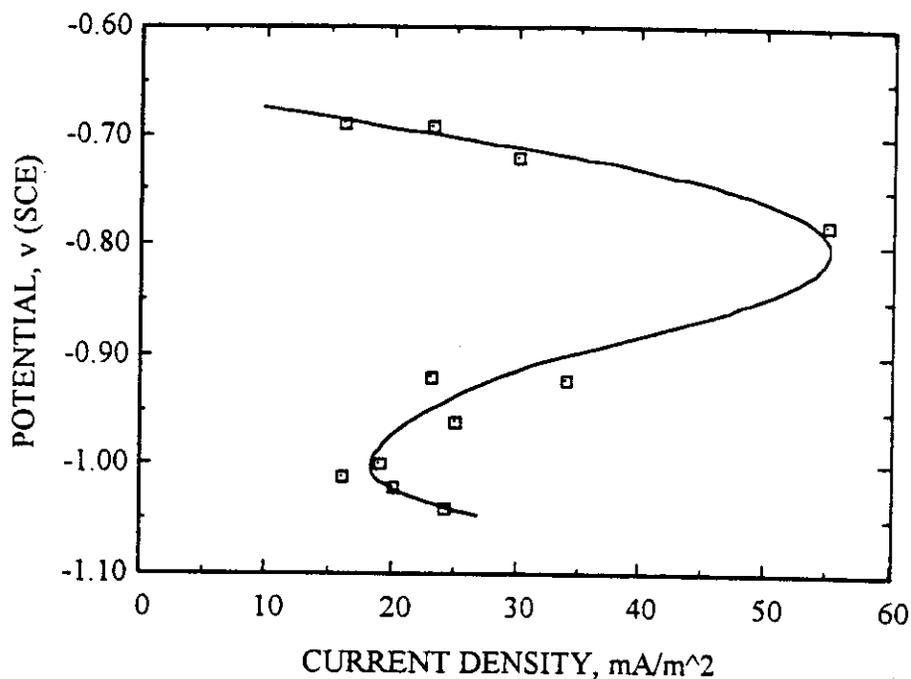
Figure 5: Long-term ϕ-i relationship for steel in sea water as determined from laboratory experiments.

The trend in Figures 4 and 5, where current density increased with increasing cathodic polarization for potentials below about -1.00 v, was attributed to the hydrogen reaction (Equation 2). Thus, the optimum situation is one where the steady-state potential of protected structures is in the range -0.90 to -1.05v.[1]

Any comprehensive effort to advance marine cathodic protection practice must include an improved understanding of the long-term ϕ-i relationship (Figure 4), the variables upon which it depends, and how and why it evolves. To this end, it is generally recognized that the minimum maintenance current density that results in the potential range -0.90 to -1.05 v is a consequence of formation of a particularly protective calcareous deposit (11-17). Such deposits occur as a consequence of reactions 1 and 2 displacing the inorganic carbon equilibria, as expressed by the reactions

$$CO_2 + H_2O \rightarrow H_2CO_3,$$ (7

$$H_2CO_3 \rightarrow HCO_3^- + H^+, \text{ and}$$ (8

$$HCO_3^- \rightarrow CO_3^{2-} + H^+,$$ (9

to the right such that pH in the vicinity of the cathode is increased and calcium and

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[1] The potential axis in Figures 4 and 5 and in other data representations to follow is referenced to the saturated calomel electrode (SCE). Because only a few millivolts separate this from the Ag/AgCl electrode, no distinction has made between the two.

magnesium rich compounds precipitate according to

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow \text{ and} \tag{10}$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \downarrow . \tag{11}$$

Presumably, the observation that potentials in the range from -0.90 to -1.05 v result in the most protective deposits (that is, in ones that are most impermeable to oxygen ingress such that current density is minimum) is caused, on the one hand, by those that form at more positive potentials being relatively thin and at more negative potentials becoming dislodged by hydrogen gas generation (Equation 3). It is also possible that deposits which form outside the above potential range have a different composition or microstructure, or both, and less protective properties. With increasing water velocity, thickness of the outer $CaCO_3$ layer decreases and, hence, oxygen availability and the current density to maintain a given cathodic potential increase (11). Also, as temperature decreases, the tendency for $CaCO_3$ formation decreases, its phase structure transitions to calcite, and a relatively porous, voluminous, unprotective $Mg(OH)_2$ occurs instead (43). Accordingly, the shape of the steady-state ϕ-i curve (Figure 5) may be significantly affected by velocity and temperature. Figure 6 illustrates the range of ϕ-i behavior that has been reported for different film formation conditions (velocity and temperature) (44).
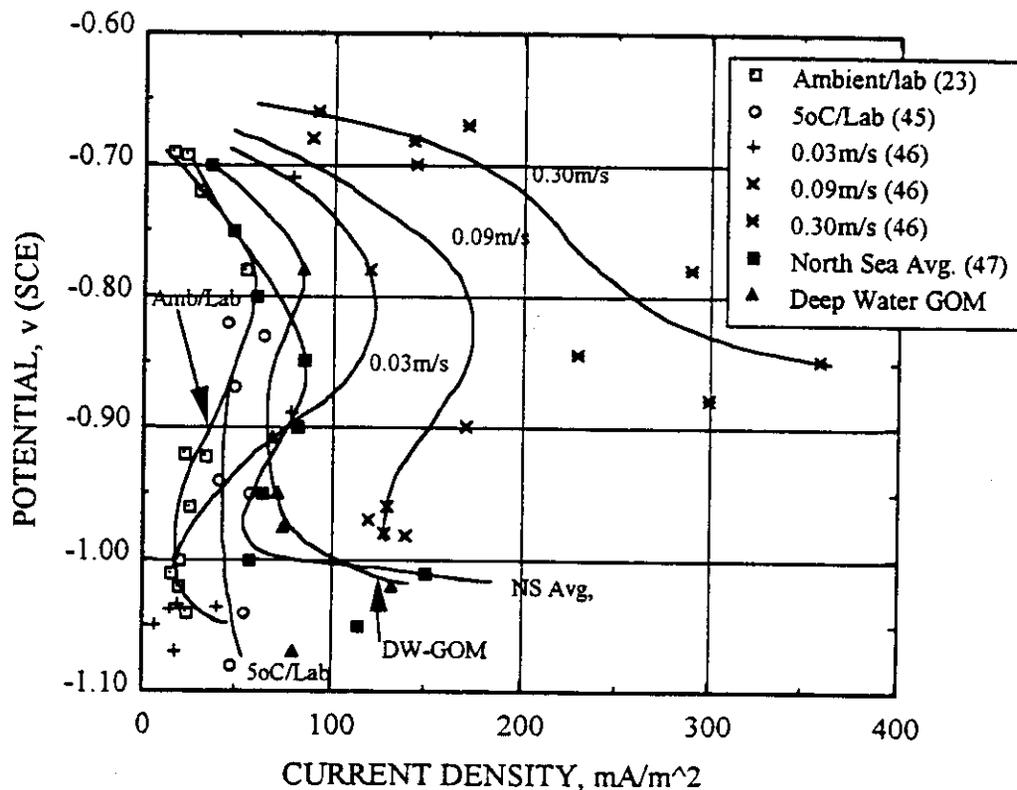
Figure 6: Long-term ϕ-i data from both laboratory and field exposures from different ocean locations.

12

The Slope Parameter Method

<u>Analytical Representation of Polarization Data</u>. In an attempt to quantify the above polarization behavior, Fischer et al. (20) considered the interrelationship between ϕ_a and ϕ_c in terms of the anodic or cathodic current (I_a or I_c, respectively) according to Ohm's law as

$$I_a = I_c = \frac{\phi_c - \phi_a}{R_x + R_c + R_a},$$

12)

where R_c is the cathode resistance. In effect, this is a generalization from which Equation 4 was developed (see Figure 3 also). Upon rearranging,

$$\phi_c = \left(R_x + R_c + R_a\right)\cdot I_c + \phi_a,$$

13)

from which the dependence of ϕ_c upon I_c is seen to be linear, assuming that the resistance terms and ϕ_a are constant. Recognizing that

$$I_c = i_c \cdot A_c,$$

14)

and

$$R_t = R_x + R_c + R_a,$$

15)

where R_t is the total circuit resistance, then

$$\phi_c = \left(R_t \cdot A_c\right)\cdot i_c + \phi_a.$$

16)

Thus, the interdependence between cathode potential and current density is projected to be linear with slope $R_t \cdot A_c$, termed the slope parameter, S, and vertical intercept equal to the product of the total circuit resistance and anode resistance, respectively, provided these parameters are constant. For space frame type structures with multiple galvanic anodes,

$$S = \frac{R_a \cdot A_c}{N}.$$

17)

Although the limited data developed by Fischer et al. (20), which were from field exposures, were mixed with regard to confirming appropriateness of Equation 16, other investigators have, in the interim, substantiated this relationship from both laboratory (23,24) and field (48) studies.

<u>A Unified Design Equation</u>. Several authors (24-26) have recently proposed that the approach to marine cp design documented in the current recommended practices (7,8) can be improved upon by combining the slope parameter term (Equation 17) with Equation 6. Thus,

$$R_a \cdot w = \frac{i \cdot T \cdot S}{C}.$$ (18

Application of Equation 18 to a particular design situation requires that a value for S be specified, as discussed subsequently. Once this is done, all terms on the right side are known from the design choices; and so the process is reduced to determination of the optimum combination of R_a and w. This may be accomplished in terms of anodes of standard dimensions or, alternately, by elongated anodes or by dualnodes (27). As an example, if anode resistance is represented in terms of Dwight's modified equation (7,8,32),

$$R_a = \frac{\rho}{2\pi L} \cdot \left[\ln\left(\frac{4L}{r}\right) - 1 \right],$$ (19

where

ρ = electrolyte resistivity,
L = anode length, and
r = anode radius,

then the left side of Equation 18 becomes

$$R \cdot w = \frac{\rho \cdot \rho' \cdot r^2 \cdot v}{2} \left[\ln \frac{4L}{r} - 1 \right],$$ (20

where

ρ' = anode density, and
v = volume fraction of the anode that is sacrificial metal as opposed to core.

The required number of anodes can then be calculated from Equation 17.

Hartt and Chen projected that the slope parameter based design approach yields a 32 percent reduction in anode mass in the case of typically sized structures (24) compared to design according to present recommended practices (7,8). This arises because Equation 18 is first principles based and incorporates both i_m and i_o. Thus, the former term is explicitly included and the latter implicitly via the slope parameter. As such, design can be optimized in terms of both parameters instead of just one. An alternative view of this point is that, of the two terms on the left side of Equation 18, R_a determines i_o while w relates to i_m.

The choice of S in Equation 18 requires either that results from prior experience for cp installations at or near the site of interest be available or that specimens be deployed and monitored for the extent to which they polarize. Figure 7 reproduces the long-term sigmoidal ϕ-i curve from Figure 5 and superimposes upon this four alternative slope parameter choices. A design according to S_1 results in inadequate protection, since the

14

polarized potential does not achieve the minimum value for arrestment of corrosion (-0.80 v). Slope parameter S_2 provides marginal protection but at a potential for which current density is relatively high. Slopes from S_3 to S_4, however, result in polarization to the potential range where i_m is minimum. It has also been demonstrated how the slope parameter can be instrumental in 1) projection of remaining cathodic protection system life (24), 2) design of retrofit cathodic protection systems (49), and 3) design of cathodic protection systems for members and components with a complex geometry (50).
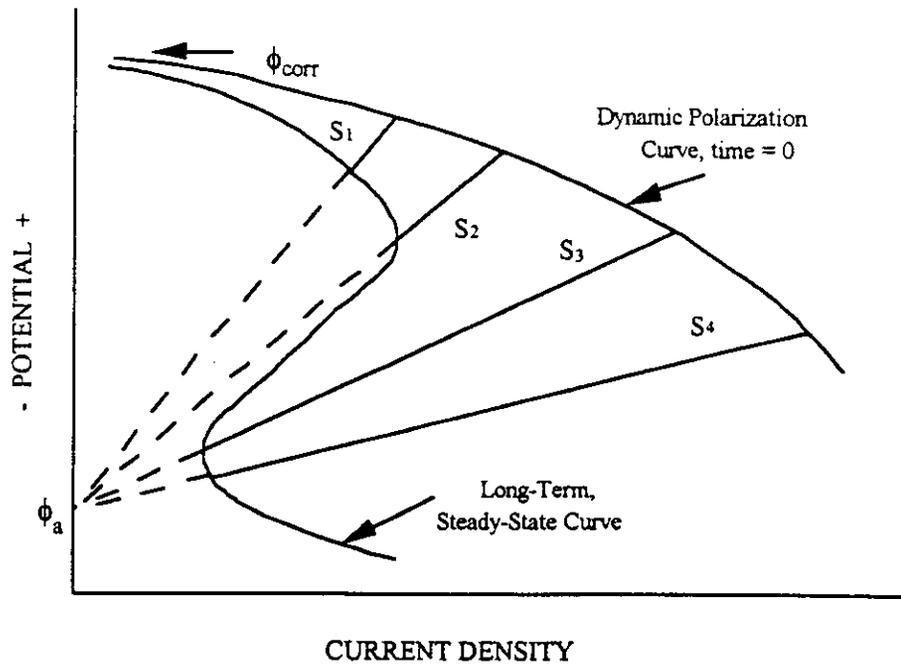
Figure 7: Alternative choices for the slope parameter and their
relationship to the initial and final ϕ-i state

Cathodic Protection Design of Marine Pipelines

Design of cathodic protection systems for marine pipelines is often based upon what has been done in the past rather than upon sound, proven scientific and engineering principles. As such, there exists uncertainty regarding the useful like of the cp system on many pipelines that are presently in place. These designs have become more conservative in recent years in that earlier practice utilized a 388 m (one-quarter mile) anode spacing, whereas 244 m (400 feet) is presently more typical. The latter allows for protection being maintained if some anodes are lost during pipeline installation, as sometimes occurs. Thus, the above comment regarding useful life uncertainty applied in particular to older lines. The sole analytical treatment that has been available historically is based upon the potential attenuation equation of Uhlig (51). Thus, for a pipeline protected by multiple, equally spaced anodes

$$E_z = E_B \cdot \cosh\left[\left(\frac{2\pi r_p R_L}{k\xi}\right)^{1/2} \cdot \left(z - \frac{L}{2}\right)\right],$$ (21)

where

E_z is potential as a function of distance z from an anode,
E_B is potential midway between anodes,
r_p is pipe radius,
R_L metalic pipe resistance per unit length,
k is a constant related to coating defect density,
ζ is coating resistivity, and
L is the one-half anode spacing.

Relatedly, anode current output, I_a, is

$$I_t = \left(\frac{2E_B}{R_L}\right) \cdot \sqrt{\left(\frac{2\pi r_p \cdot R_L}{k\zeta}\right)} \cdot \sinh\left[L \cdot \sqrt{\left(\frac{2\pi r_p \cdot R_L}{k\zeta}\right)}\right].$$ (22)

More recently, boundary element modeling has evolved as a viable tool for cp design of marine structures, including pipelines. Also, Pierson et al. (52) developed a first principles based expression for potential attenuation along a pipe as

$$E_c''(z) + E_c'(z) \cdot \frac{H}{2} \cdot \left(\frac{1}{r_a} - \frac{1}{z}\right) + E_c(z) \cdot \left(\frac{H}{z^2} - B\right) = 2H \cdot \frac{1}{z^3} \cdot \int_z^L E(z)dz,$$ (23)

where

$$H = \frac{\rho_e \cdot r_p}{\alpha \gamma} \text{ and}$$

$$B = \frac{R_L \cdot 2\pi r_p}{\alpha \gamma}.$$

with r_a being the radius of a spherical anode superimposed upon the pipe at $z = 0$ (alternatively, r_a can be viewed as the equivalent radius of a non-spherical anode). While this expression must be solved numerically, a closed form solution was provided based upon the assumption $z >> r_a$ as

$$\frac{E_c(z)}{\Delta\phi_o} = e^{\lambda_2 \cdot z} + \frac{\left(e^{\lambda_1 \cdot z} - e^{\lambda_2 \cdot z}\right)}{\left[1 - \left(\frac{\lambda_1}{\lambda_2}\right) \cdot e^{L \cdot (\lambda_1 - \lambda_2)}\right]},$$ (24)

where $\Delta\phi_o$ is the open circuit anode-cathode potential difference and

16

$$\lambda_1 = \frac{-P_1 + \sqrt{P_1^2 - 4 \cdot P_2}}{2}$$

and

$$\lambda_2 = \frac{-P_1 - \sqrt{P_1^2 - 4 \cdot P_2}}{2}$$

with

$$P_1 \equiv \frac{r_p}{r_a} \cdot \frac{\rho_e}{\alpha \gamma}$$

and

$$P_2 \equiv \frac{-R_m \cdot 2\pi r_p}{\alpha \gamma},$$

where $\square$ is the slope of the cathodic polarization curve, which was assumed to be linear, and $\square$ is the ratio of total surface area to that which is bare. Figures 8-11 show potential profiles based upon 1) Equation 21, 2) Equation 24, and 3) boundary element modeling (BEM) for the case of a 0.271 m diameter pipeline with r_a = 0.181 m and L = 122 m assuming $\square\square_o$ = 0.4, and $\square\square$ values of 4, 8, 20, and 100. Also shown in the case of Equation 24 are solutions for three different r_a values, where the largest of these corresponds to the equivalent radius of a 0.187 m radius standard bracelet anode (initial dimensions) and the latter two to the size at 50 and 100 percent depletion. These figures show that the Uhlig expression (Equation 21) yields the least conservative results and BEM the most conservative.

Pierson et al. (52) also provided a first principles based analysis of how the electrolyte (anode) and metallic resistance terms should vary along a pipe length. The results are shown in Figure 12 for the specific case of r_p = 0.271 m, r_a = 0.181 m, $\square_e$ = 0.3 $\square$.m, metallic resistivity = 17.10^{-8} $\square$.m, $\square\square$ = 100, and $2L$ = 10 km from which three zones are apparent as listed below:

1. The first several meters from the anode. It is here that the change in electrolyte resistance per unit pipe length is greatest. Note the corresponding change in pipeline potential to more positive values that occurs in this same range according to the BEM results (see Figures 8-11).

2. From the first several meters of the anode to approximately 10^3 meters. Here both resistance and potential are essentially constant (BEM analysis results).

3. Beyond 10^3 meters. In this regime pipeline resistance becomes increasingly

17
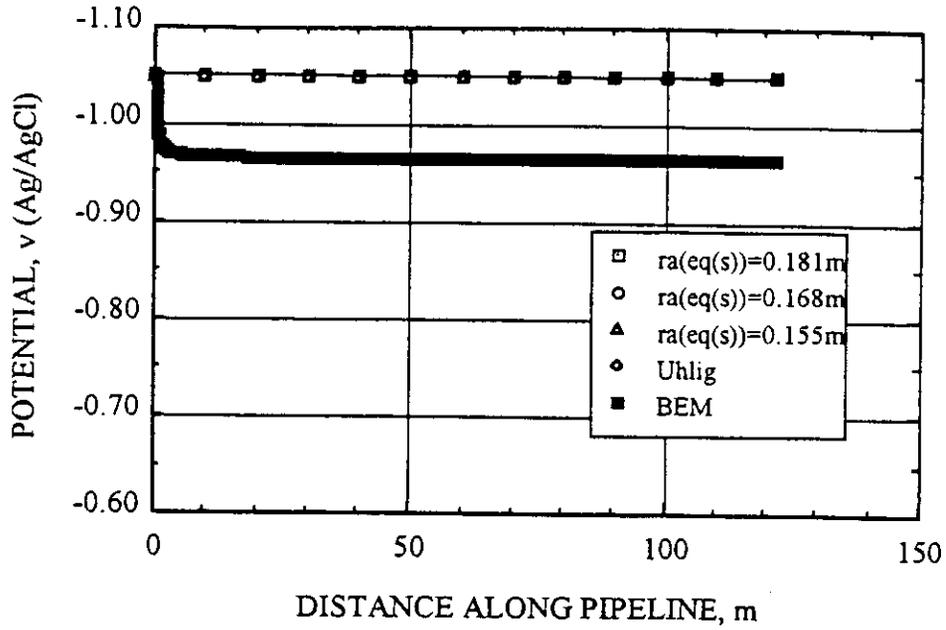
Figure 8: Comparison of attenuations for the three approaches for $2L = 244$ m and $\alpha\gamma = 100$.
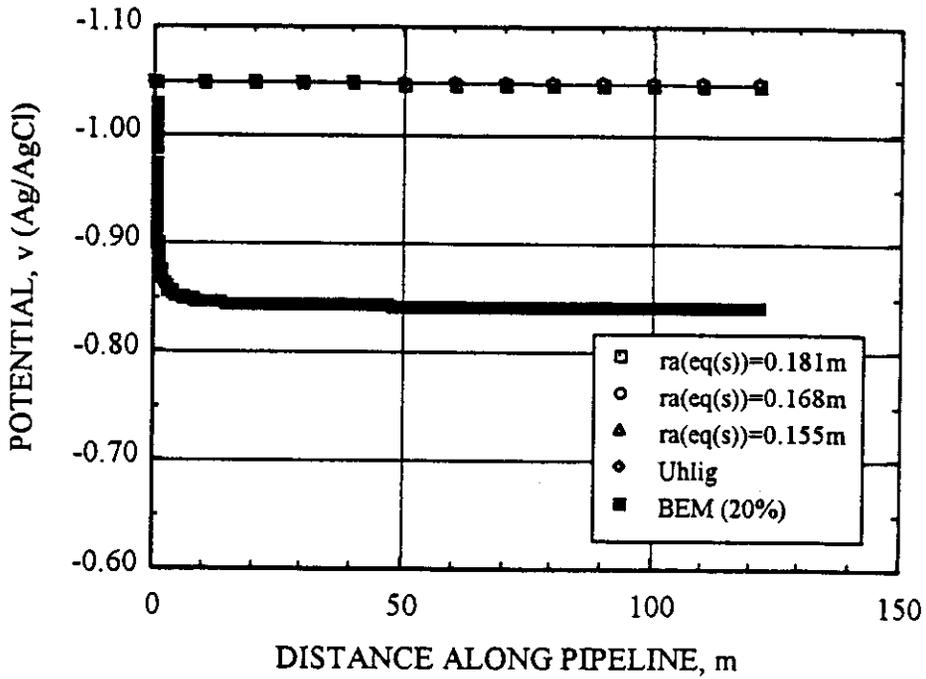
Figure 9: Comparison of attenuations for the three approaches for $2L = 244$ m and $\alpha\gamma = 20$.
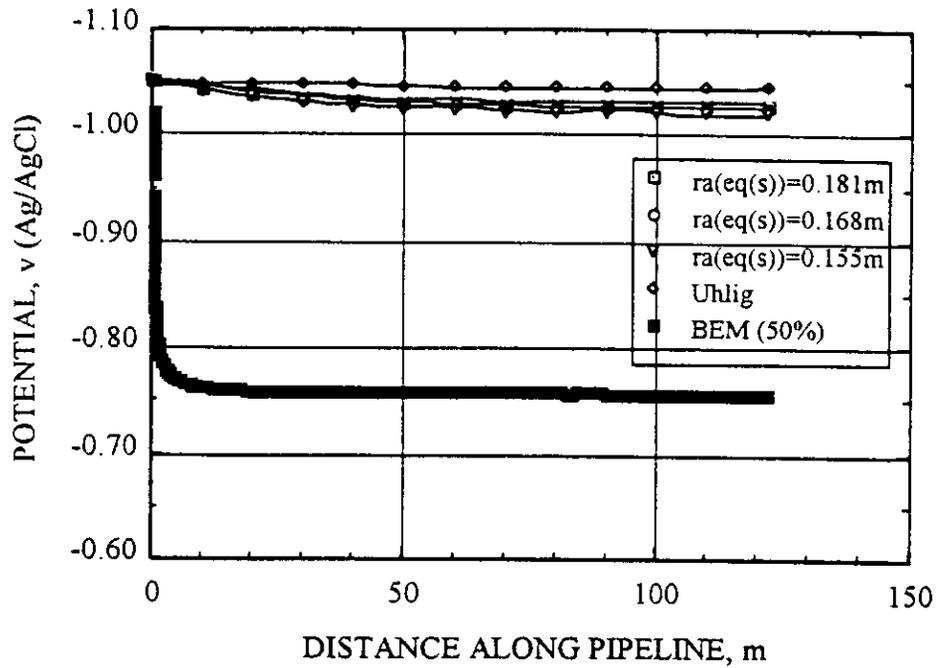
Figure 10: Comparison of attenuations for the three approaches for $2L = 244$ m and $\alpha\gamma = 8$.
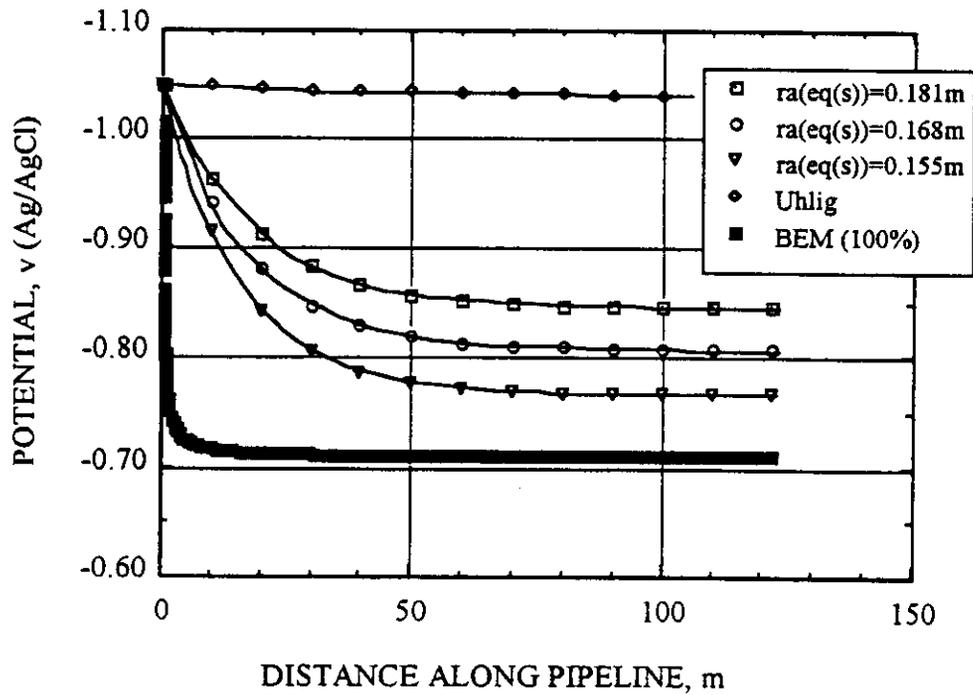
Figure 11: Comparison of attenuations for the three approaches for $2L = 244$ m and $\alpha\gamma = 4$.
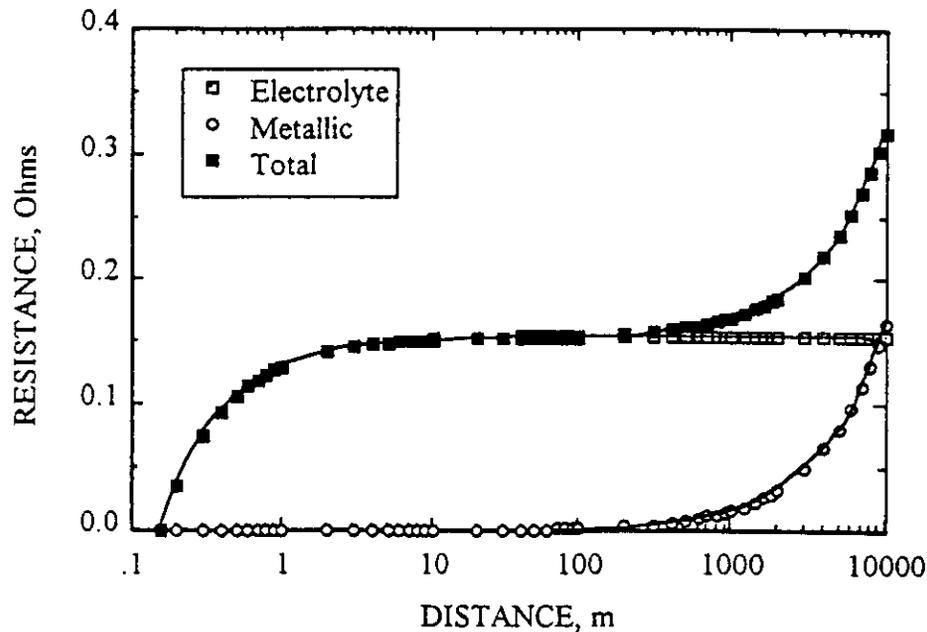
Figure 12: Resistance as a function of distance, as this occurs in the
electrolyte and metal pipe. Net resistance is also shown.

important. This zone is not apparent from the analyses in Figures 8-11 because these pertained to a pipeline with a 244 m anode spacing only.

Because of the one-to-one correspondence between resistance (Figure 12) and potential as projected by BEM (Figures 8-11), it was concluded that the BEM analysis results were the most accurate of the three methods. On this basis, the Uhlig equation provided the least accurate solution because it considers only coating and metallic resistance but not that of the electrolyte. Lack of agreement between the Equation 24 and BEM results apparently occurred because imposition of the $z >> r_a$ criterion in arriving at Equation 24 voids disclosure of the steep resistance and, hence, potential gradient in the immediate vicinity of the anode. Presumably, agreement between the BEM and the first principles based relationship could be achieved by solving Equation 23 numerically. In lieu of this, improved accuracy compared to the Uhlig expression can be achieved by employing Equation 23 instead; however, both solutions are apparently non-conservative.

Remaining Challenges – Space Frame Structures

With the advent of the first principles based slope parameter approach to cp design, the remaining issue that requires resolution before cathodic protection systems can be better designed is development of improved procedures for specifying the parameters on the right side of Equation 18, namely S, i_m, and C, where the former two relate to polarization characteristics of the structure and the latter to galvanic anode performance. Also, the accuracy whereby anode resistance (R_a) is determined, normally using the modified Dwight equation (7,8,32)) is uncertain. With regard to the first of the above terms (S or, alternatively, initial current density), it is noteworthy that there presently

20

exists no first principles based method for defining this parameter in the case of a specific design (this choice is presently made based upon either past experience or by test panel exposures). However, it is projected that improved insight into selection of i_m and C is more critical. In the case of i_m, present Recommended Practices (7,8) list this parameter as 55-80 mA/m^2 for near surface sub-tropical regions; however, values of 3.4 and 8.8 mA/m^2 have been reported for two Gulf of Mexico structures (ages 19 and 22 years, respectively) (48) and 5.4-34.4 mA/m^2 for 15 Arabian Gulf ones (ages 13-26 years) (53). Since anode mass to achieve a particular design is directly proportional to i_m, significant cost savings can potentially result if, indeed, design according to a reduced current density can be justified.

<u>Considerations Regarding Mean Current Density</u>. Hartt and Lemieux (54) have recently evaluated current density data from both offshore structures and long-term laboratory and field exposures, to the extent that such information is available, for the purpose of determining i_m. Figure 13 shows the results from this, where the data have been partitioned according to warm (a) and cold (b) water exposure. The structures represented here include exposures to different oceans and to both shallow and deep and tropical/temperate and northern latitude locations. A scatter band for the cold water data is superimposed upon the warm water plot and visa versa; and it is apparent from this that, although the two data sets are within the same range in the short term (10-10^4 hours), current density at greater times for most of the structures in warm water locations falls below that for cold water ones. Presumably, this is a consequence of the greater tendency for calcareous deposit formation in the former compared to the latter (43). The general trend, both for the data collectively and for individual structures, consists of an initial period during which current density was roughly constant (this occurred in some but not all cases) followed by decay according to a power law relationship (linear on log-log coordinates). Also, this current density decay was continuous, albeit at a progressively reduced rate, such that there is no indication of a true steady-state value being ultimately achieved.

Curve filling to the two data sets (Figures 8a and b) led to the equation

$$i_m = \frac{10^{(a+c\sigma)} \cdot T^b}{b+1},$$
(25

where σ is the standard deviation, a and b are constants, and c is a multiplicant which reflects a factor of safety in the design. Values for the former three terms in each of the two types of exposure (warm and cold water) are given in Table 2.

It was proposed that this expression serve as the basis whereby values for i_m are specified in design. The choice of c can vary depending upon the degree of conservativism that is considered appropriate or the extent to which data exist for the specific site in question. In this regard, c need not be a whole number. Table 3 tabulates specific i_m values for both warm and cold water exposures and for $c = 0$, +1, and +2.. Thus, a major
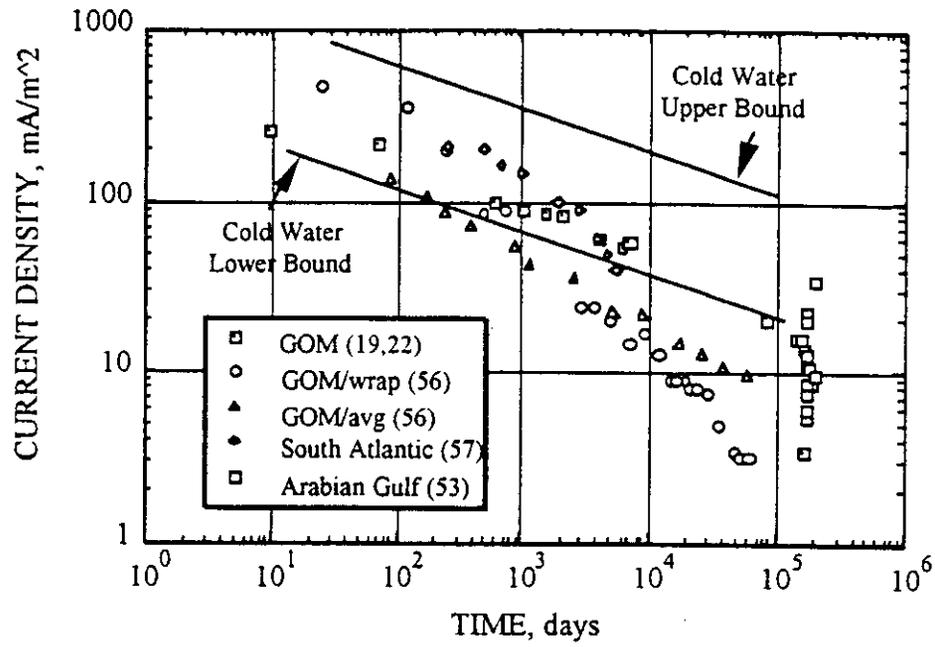
(a)
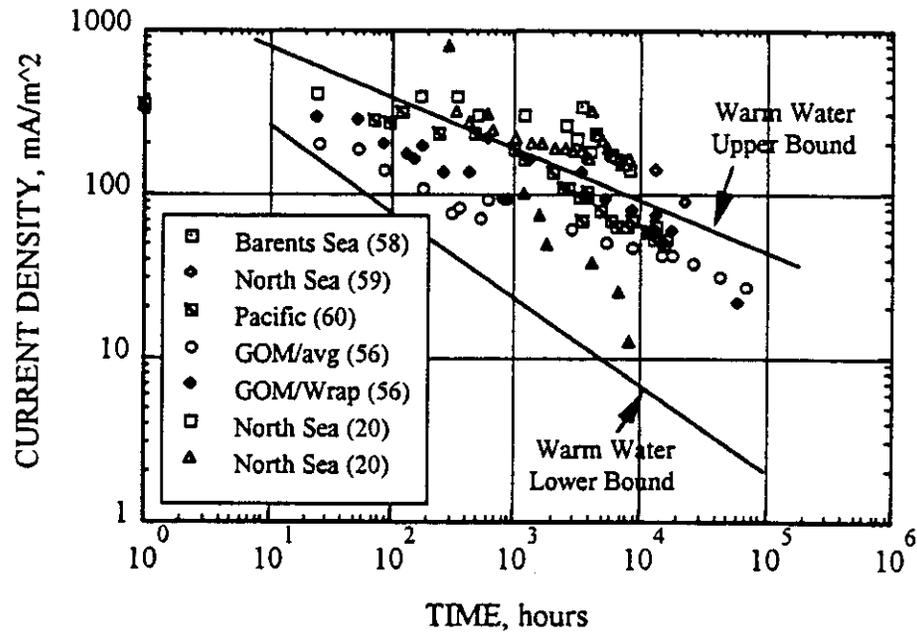
(b)

Figure 13: Current density versus exposure time for offshore structures in (a) warm and (b) cold waters.

Table 2: Curve-fitting parameters for Equation 21.

	Warm/Shallow Parameters	Cold/Deep Water Parameters
s	0.233	0.229
a	3.130	2.820
b	-0.410	-0.226

component of the proposed procedure is that i_m is a function of the design life. These results indicate that, for a 20 year design life, the mean+2$\square$ value for i_m differs from the recommended Gulf of Mexico one (8) by less than 10 percent, while the mean+1$\square$ value is about one-half of this. The mean itself, on the other hand, is approximately 30 percent of the presently recommended value. In the cold water case, these same three values range from approximately 50 percent greater to about the same to 50 percent below the

Table 3: List of i_m values as a function of T and for different degrees of design conservativism.

Time, years	Mean Current Density, mA/m^2					
	c= 0		c= 1		c= 2	
	Cold/Deep	Warm	Cold/Deep	Warm	Cold/Deep	Warm
1	109	55	185	95	314	162
5	76	29	129	49	218	84
10	65	22	110	37	186	63
15	59	18	100	31	170	53
20	56	16	94	28	159	47
25	53	15	89	25	151	43
30	51	14	86	23	145	40

present North Sea design value for i_m (8) for the same degrees of conservativism (mean+2$\square$ $\square$$\square$ mean+1$\square$, and mean i_m, respectively). Additional long-term data are needed in order to establish greater confidence in this procedure.

Considerations Regarding Anode Current Capacity. Insight regarding anode current capacity is limited by the lack of availability of truly long-term data. Thus, while laboratory tests exist for measuring this parameter in the short-term (7,61), such procedures are intended as a quality control tool rather that a performance predictor. However, results from such tests often are used for the latter purpose (performance prediction). Two examples of long-term data that are relevant to the present discussion are those from, first, the laboratory and field tests of Espelid et al. (62), which extended from 0.5 to 2.5 years, and, second, the measurements of Kiefer et al. (53) on 15 Gulf of Arabia structures whose age ranged from 13 to 26 years. Also, the data reported by Kennelley and Mateer (49) for two Gulf of Mexico structures permit current capacity to
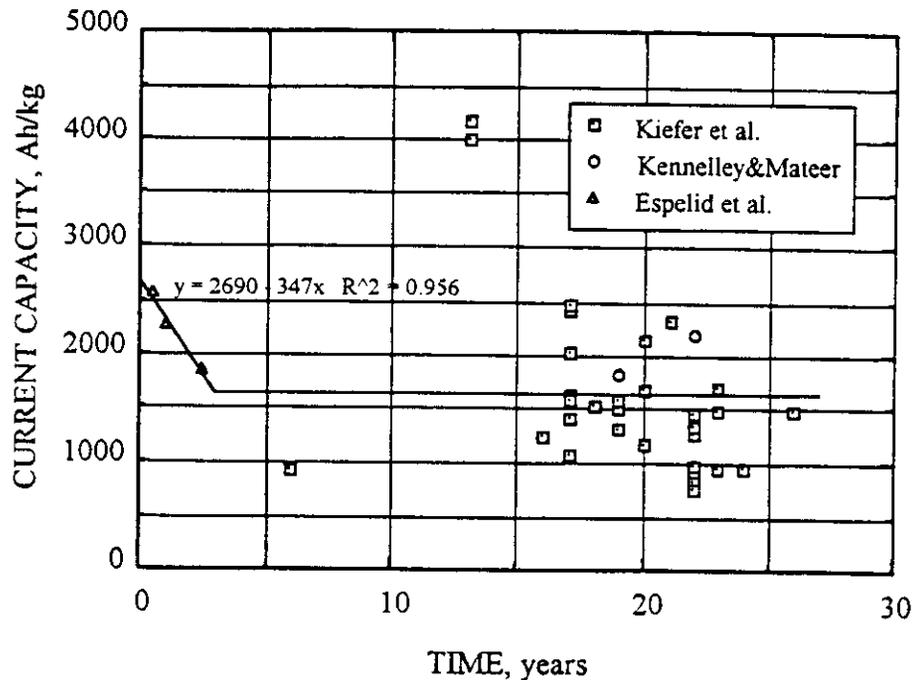
Figure 14: Anode current capacity as a function of time based upon laboratory and field testing and data from offshore structures.

be determined for the anodes on these as well. The results from this analysis are shown in Figure 14, where each datum reflects the time average value for C after the indicated age. Thus, the results from the tests of Espelid et al. (62) indicate that C decreased with time at a rate of 35 Ah/kg per year. Scatter for the data from actual structures is relatively high, presumably because anode weight loss determinations were based upon diver estimate or measurement of anode dimensions such that a relatively large inaccuracy is not unexpected. It evaluating these data, it was assumed that C was invariant with time after approximately three years. While numerous factors, including 1) composition, 2) microstructure, 3) current density, and 4) exposure conditions, are known to affect anode performance, it may be that time is the most important factor in the long-term. A possible explanation for this is that pH beneath the corrosion products that ultimately develop on aluminum base anodes has been measured as 3.8-4.5 (62), such that acidification and activity of local action low overvoltage hydrogen reaction sites may become controlling. The fact that structures with both Sn and In activated anodes are represented in the Figure 14 data is consistent with this.

Of importance within the present context is that the long-term time average C in Figure 14 is 1,646 Ah/kg, where the design values in the Recommended Practices are 2,000 (7) 2,750 (8) Ah/kg, respectively. This suggests that as far as this parameter alone is concerned, under design is being affected by either 18 or 40 percent. Also, if the data scatter in Figure 14 is real, then structure to structure anode performance is highly variable.

Summary. While the first principles based slope parameter (Equations 18) provides an improved protocol for cp design compared to what was available before this (51), uncertainty regarding 1) how values for S are determined and 2) design values for i_m and C leads, in turn, to a lack of confidence in the overall procedure. While this uncertainty has not been a major factor in the past because of, first, cp system over design and, second, lack of major penalties in cases of failure and premature retrofit, it becomes of increased importance in the case of deep water and frontier structures. Consequently, it is timely that the issue of long-term anode performance and structure current demand, in particular, be addressed and, accordingly, that a greater understanding of the cp design process be gained.

Remaining Challenges – Pipelines and Risers

Cathodic protection design for marine pipelines and risers is technically more challenging and the practice less mature than for space frame structures. Presently lacking are 1) simple, confirmed-as-accurate analytical representations of potential attenuation and for anode current output. With such information, a technically sound cp design protocol can be established. Necessary input regarding such a protocol includes 1) coating breakdown factors and 2) the same parameters that remain in question in the case of space frame structures (in particular, long-term current demand and anode current capacity).

Conclusions

While marine cathodic protection technology has in the past evolved lethargically and has relied largely upon what was done in the past, present and evolving activities in deep water and frontier areas require that corrosion control be both efficient and highly reliable. Consequently, findings in the past one-to-two decades have given insight into rapid polarization, which is now part of the Recommended Practices. Also, the slope parameter method is still evolving; and this affords the promise that cp design can become first principles based. Remaining issues include uncertainty regarding 1) mean current density and 2) anode current capacity. On the other hand, cathodic protection of marine pipelines and risers is more complex than for space frame structures and, consequently, the technology here is less mature. As such, no proven analytical tool for straightforward representation of potential attenuation and anode current output is available (boundary element modeling is considered too complex to satisfy this). Also, the same uncertainties that applied to space frame structures (definition of long-term current demand and anode current capacity) apply here also. It is projected that with a concerted effort, a first principles based protocol for marine cathodic protection design, as this applies to space frame structures and to pipelines and risers, can be developed. For the former (space frame structures) this can be accomplished in five years and for the latter (pipes and risers) ten years.

Bibliography

1. Davy, H., *Phil. Trans. Royal Soc. London*, Vol. 114, 1824, p.151.

2. Davy, H., ibid, Vol. 114, 1824, p.242.

3. Davy, H., ibid, Vol. 115, 1825, p.328.

4 Graham, D. P., Cook, F. E. and Preiser, H. S., *Trans. Soc. Naval Arch. and Marine Engrs.*, vol. 64, 1956, p.241.

5. Peterson, M. H., "A Short History of Marine Cathodic Protection", paper no. 285 presented at CORROSION/86, March 17-21, 1986, Houston.

6 Thomas, E. D., Lucas, K. E., Foster, Parks, R. L., and Kaznoff, A. I., "Physical Scale Modeling of Impressed Current Cathodic Protection Systems", paper no. 274 presented at CORROSION/89, April 17-21, 1989, New Orleans.

7. "Cathodic Protection Design," *DnV Recommended Practice RP401*, Det Norske Veritas Industri Norge AS, 1993.

8. "Corrosion Control of Steel-Fixed Offshore Platforms Associated with Petroleum Production", *NACE Standard RP 0176-94*, NACE International, Houston, 1994.

9. Uhlig, H. H. and Revie, R. W., *Corrosion and Corrosion Control*, Third Ed., J. Wiley and Sons, New York, 1985, pp. 223-228.

10. Cox, G. C., "Anticorrosive and Antifouling Coating and Method of Application", U.S. Patent 2,200,469, 1940.

11. Wolfson, S. L. and Hartt, W. H., *Corrosion*, vol. 37, 1981, p. 70.

12. Hartt, W. H., Culberson, C. H. and Smith, S. W., *Corrosion*, vol. 40, 1994, p. 609.

13. Lin, S-H and Dexter, S. C., *Corrosion*, vol. 44, 1988, p. 615.

14. Finnegan, J. E. and Fischer, K. P., "Calcareous Deposits: Calcium and Magnesium Ion Concentrations," paper no. 581 presented at CORROSION/89, April 17-21, 1989, New Orleans.

15. Fischer, K. P. and Finnegan, J. E., "Cathodic Protection Behavior of Steel in Sea Water and the Protective Properties of the Calcareous Deposits," paper no. 582 presented at CORROSION/89, April 17-21, 1989, New Orleans.

16. Luo, J. S., Lee, R. U., Chen, T. Y., Hartt, W. H. and Smith, S. W., *Corrosion*, vol. 47, 1991, p. 189.

17. Mantel, K. E., Hartt, W. H. and Chen, T. Y., *Corrosion*, vol. 48, 1992, p. 489.

18. Foster, T., and Moores, V. G., "Cathodic Protection Current Demand of Various Alloys in Sea Water," paper no. 295 presented at CORROSION/86, March 17-2, 1986, Houston.

19. Mollan, R. and Anderson, T. R., "Design of Cathodic Protection Systems," paper no. 286 presented at CORROSION/86, March 17-2, 1986, Houston.

20. Fischer, K. P., Sydberger, T. and Lye, R., "Field Testing of Deep Water Cathodic Protection on the Norwegian Continental Shelf," paper no. 67 presented at CORROSION/87, March 9-13, 1987, San Francisco.

21. Fischer, K. P. and Finnegan, J. E., "Cathodic Protection Behavior of Steel in Sea Water and the Protective Properties of the Calcareous Deposits," paper no. 582 presented at CORROSION/89, April 17-21, 1989, New Orleans.

22. Schrieber, C. F. and Reding, J., "Application Methods for Rapid Polarization of Offshore Structures," paper no. 381 presented at CORROSION/90, April 23-27, 1990, Las Vegas.

23. Wang, W., Hartt, W. H., and Chen, S., *Corrosion*, vol. 52, 1996, p. 419.

24. W. H. Hartt, Chen, S., and Townley, D. W., *Corrosion*, vol. 54, 1998, p 317.

25. Townley, D. W., "Unified Design Equation for Offshore Cathodic Protection," paper no. 97473 presented at CORROSION/97, March 9-14, 1997, New Orleans.

26. "Design of Galvanic Anode Cathodic Protection Systems for offshore Structures," NACE International Publication 7L198, NACE International, Houston, Texas, July, 1998.

27. Burk, J. D., "Dualnode Field Performance Evaluation – Cathodic Protection for Offshore Structures," paper no. 309 presented at CORROSION/91, March 11-14, 1991, Cincinnati.

28. Andersen, T and Misund, A., "Pipeline Reliability: An Investigation of Pipeline Failure Characteristics and Analysis of Pipeline Failure Rates for Submarine and Cross-Country pipelines," J. Pet. Technology, April, 1983, p. 709.

29. "Analysis of the MMS Pipeline Leaks Report for the Gulf of Mexico," Texaco USA, 133 W. Santa Clara, Ventura, CA 93001, October 25, 1985.

30. Mandke, J. S., "Corrosion Causes Most Pipeline Failures in the Gulf of Mexico," Oil and Gas Journal, October 29, 1990, p. 40.

31. Weldon, C. and Kroon, D., "Corrosion Control Survey Methods for Offshore Pipelines," Proceedings International Workshop on Offshore Pipeline Safety, New Orleans, Dec. 4-6, 1991, p. 196.

32. Dwight, H. B., *Electrical Engineering*, Vol. 55, 1936, p. 1319.

33. Sunde, E. D., *Earth Conduction Effects in Transmission Systems*, Dover Publications, Inc., New York, 1968.

34. McCoy, J. E., *Transactions Institute of Marine Engineers*, Vol. 82, 1970, p. 210.

35. Cochran, J. C., "A Correlation of Anode-to-Electrolyte Resistance Equations Used in Cathodic Protection," paper no. 169 presented at CORROSION/82, March 22-26, 1982, Houston.

36. Strommen, R., *Materials Performance*, Vol. 24(3), 1985, p. 9.

37. Sunde, E. D., *Earth Conduction Effects in Transmission Systems*, Dover Publications, Inc., New York, 1968, p. 72.

38. Cochran, J. C., "Additional Anode-to-Electrolyte Resistance Equations Useful in Offshore Cathodic Protection," paper no. 254 presented at CORROSION/84, April 2-6, 1984, New Orleans.

39. "Corrosion Control of Steel-Fixed Offshore Platforms Associated with Petroleum Production", *NACE Standard RP 0176*, NACE, Houston, 1976.

40. Evans S., "Use of Initial Current Density in Cathodic Protection Design", *Material Performance*, Feb. 1988, Vol. 27(2), p. 9.

41. Cochran, J. C., "New Mathematical Models for Designing Offshore Sacrificial Cathodic Protection Systems", paper no. 3858, *Proceedings 1980 Offshore Technology Conference*, May 5-8, 1980, Houston.

42. Cox, G. C., "Anticorrosive and Antifouling Coating and Method of Application", U.S. Patent 2,200,469, 1940.

43. Hartt, W. H., Kunjapur. M. M., and Smith, S. W., *Corrosion*, Vol. 43, 1987, p. 674.

44. Hartt, W. H., "Historical Development, Present Understanding, and Future Considerations Regarding Cathodic Protection of Offshore Structures," Plenary Lecture to be presented at the Eight Middle-East Corrosion Conference, May 18-20, 1998, Bahrain.

45. Chen, S. and Hartt, W. H., Center for Marine Materials, Florida Atlantic University, Boca Raton, Florida 33431, unpublished research.

46. Hugus, D. and Hartt, W. H., "The Effect of Velocity upon Maintenance Current Density for Cathodically Polarized Steel in Sea Water," paper no. 98726 presented at CORROSION/98, March 22-27, 1998, San Diego.

47. Strommen, R. D., Osvoll, H., and Keim, W., "Computer Modeling and In-Situ Current Density Measurements Prove a Need for Revision of Offshore CP Design Criteria," paper no. 297 presented at CORROSION/86, March 17-21, 1986, Houston.

48. Kennelley, K. J. and Mateer, M. W., "Evaluation of the Performance of Bi-metallic Anodes on Deep Water Production Platform", paper no. 523 presented at CORROSION/93, March 8-12, 1993, New Orleans.

49. Hartt, W. H. and Chen, S., "Galvanic Anode Cathodic Protection of Steel in Sea Water - Part IV The Slope Parameter Approach to Retrofit Design." Accepted for publication in *Corrosion*.

50. Pierson, P. and Hartt, W. H., "Galvanic Anode Cathodic Protection of Steel in Sea Water - Part III The Slope Parameter Approach for Design for Conductor Arrays." Accepted for publication in Corrosion.

51. Uhlig, H. H. and Revie, R. W., *Corrosion and Corrosion Control*, Third Ed., J. Wiley and Sons, New York, 1985. p. 396-401.

52. Pierson, P., Hartt, W. H., and Bethune, K., "Potential Attenuation and Anode Current Output Determination Alternatives for Marine Pipelines and Risers," paper no. 99628 to be presented at CORROSION/99, San Antonio, Texas, April 25-30, 1999.

53. Kiefer, J. H., Thomason, W. H., and Alansari, N. G., "Experiences in Retrofitting Sacrificial Anodes in Offshore Arabian Gulf," paper no. 735 presented at CORROSION/98, March 22-27, 1998, San Diego.

54. Hartt, W. H. and Lemieux, E. "A Principal Determinant in Cathodic Protection Design of Offshore Structures – the Mean Current Density," paper no. 99627 to be presented at CORROSION/99, San Antonio, Texas, April 25-30, 1999.

55. Mateer, M. W. and Kennelley, K. J., "Design of Platform Anode Retrofits Using Measured Structure Current Density", paper no. 526 presented at CORROSION/93, March 8-12, 1993, New Orleans.

56. Goolsby, A. D. and Wolfson, S. L., "Extended Cathodic Protection Monitoring of One of the World's Deepest Fixed Offshore Platforms – Bullwinkle," paper no. 98733 presented at CORROSION/98, San Diego, March 22-27, 1998.

57. Baptista, W. and da Costa J. C. M., Materials Performance, Vol. 36(1), 1997, p. 9.

58. Fischer, K. P., Thomason, W. H., and Eliassen, S., The Importance of Calcareous Deposits and the Environmental Conditions," paper no. 548 presented aT CORROSION/96, March 24-29, 1996, Denver.

59. Andresen, R. E., "Cathodic protection of Steel in Sea Water: Polarizability of Steel in Artificial and Natural Sea Water," Norwegian Institute of Technology, May, 1982, Potect #160269.00.

60. Goolsby, A. D., Materials Performance, Vol 23(4), 1984, p.26.

61. "Impressed Current Laboratory Testing of Aluminum Alloy Anodes," NACE International Standard Test Method TM0190, NACE International, Houston, Texas, 1998.

62. Espelid, B., Schei, B., and Sydberger, T., "Characterization of Sacrificial Anode Materials through Laboratory Testing," paper no 551 presented at CORROSION/96, March 24-29, 1996, Denver, Colorado.
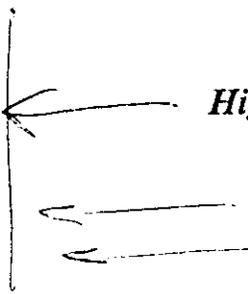
High Strength Fasteners for Seawater Immersion Service

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ABSTRACT

Alloy K-500 is the currently used high strength alloy for Navy fastener applications in immersion service. Alloy K-500 has performed well as a fastener material in seawater but is susceptible to hydrogen cracking in areas of intense cathodic polarization and is galvanically incompatible with titanium and Alloy 625 components. Due to these inadequacies, it is necessary to identify alternate fastener materials that can suitably replace Alloy K-500. Numerous alloys that meet the minimum yield strength requirements of Alloy K-500 (90 ksi) have been considered. These include titanium-base, nickel-base, and stainless steel alloys. Data and guidelines on corrosion behavior, mechanical properties, fatigue behavior, and other relevant material properties are being assembled into a high strength fastener handbook for 15 alloys. The technical information in the handbook will include data generated from in-house Navy programs as well as data reported in the literature by government and industry sources. Information included in the fastener handbook will be presented here, with particular emphasis on the applicability of specific alloys based on seawater corrosion behavior.

INTRODUCTION

In addition to meeting strength, ductility, and other mechanical property requirements, high strength fastener materials must provide adequate resistance to corrosion in the service environment of interest. High strength fasteners used on naval vessels are exposed to a variety of marine environments, including full immersion in seawater, intermittent seawater spray/marine atmosphere in topside areas, and alternate wetting in areas such as bilges. When assessing the corrosion resistance of a material, all applicable forms of corrosion must be considered. For naval fasteners, the forms of corrosion of concern include general, localized, and galvanic corrosion, along with environmentally assisted cracking (EAC), which includes hydrogen embrittlement (HE) and stress corrosion cracking (SCC). Sustained load cracking (SLC) resistance is also considered.

Corrosion data from laboratory and field tests performed on 15 alloys in simulated and natural seawater environments will be reviewed. The corrosion resistance of Alloy 725, Alloy 925, UNS N07716 (Alloys 625+ and 625PH), Alloy 718, Rene 41, MP35N, MP159, and Ti-6Al-4V (ELI), Ti 38-6-44, Ti 5111, Ti 16-2.5-3, Alloy A286, and 17-4 PH will be assessed relative to

Alloy K-500, which is considered to be the baseline material for naval fasteners immersed in seawater.

Table I presents the nominal composition, recommended heat treatment, and specification for each of the high strength fastener alloys. Table II summarizes the mechanical properties of each alloy in the recommended condition. The recommended material condition for each alloy was defined based on the minimum strength requirements of Alloy K-500.

Table I. Composition and Heat Treatment Schedules for Fastener Alloys

Alloy	Nominal Composition	Recommended Heat Treatment	Specification or Standard
K-500	Ni-30Cu-3Al	Solution Treatment + Age (either Single or Dual Age)	FED SPEC QQ-N-286, MIL-S-1222
Alloy 725	Ni-21Cr-8Mo-8Fe-3.5Cb	Solution Treatment + Dual Age[a]	ASTM B805
Alloy 925	Ni-27Fe-20Cr-3Mo-2Ti-2Cu	Solution Treatment + Dual Age	None
UNS N07716 (625+, 625PH)	Ni-21Cr-8Mo-5Fe-3.5Cb	Solution Treatment + Dual Age[a]	ASTM B805
Alloy 718	Ni-19Cr-17Fe-5Cbe-3Mo	Solution Treatment + Dual Age	ASTM B637
Rene 41	Ni-20Cr-11Co-10Mo-5Fe-3Ti	Solution Treatment + Age	AMS 5713
MP35N	35Ni-35Co-20Cr-10Mo	Solution Treatment + Cold Work + Age	AMS 5845
MP159	36Co-25-Ni-19Cr-9Fe-7Mo-3Ti	Solution Treatment + Cold Work + Age	AMS 5842
Ti-6Al-4V, Ti-6Al-4V ELI	Ti-6Al-4V	Recrystallization or Beta Anneal	MIL-H-81200, MIL-S-1222
Ti 38-6-44	Ti-3Al-8V-6Cr-4Mo-4Zr	Solution Treatment[b]	MIL-H-81200, MIL-T-9047
Ti 5111	Ti-5Al-1Sn-1Zr-1V-0.8Mo	α-β Forged (1750°F)	None
Ti 16-2.5-3	Ti-16Mo-2.5Nb-3Al	Solution Treatment + Overage	None
Alloy A286	Fe-26Ni-15Cr-2Ti-2Mn-1Mo	Solution Treatment + Age	ASTM A453
17-4 PH H1100	Fe-16Cr-4Ni-4Cu	Solution Treatment + Age	ASTM A693

[a]: identical to Age process in ASTM B805 except for furnace cooling rate; for optimum results, furnace cool at 100°F/hour.

:identical to solution treatment process in MIL-H-81200 except for temperature range (1400-1700°F in MIL-H-81200); for optimum results, heat within 1500-1550°F.

Table II. Mechanical Properties for Fastener Alloys

Alloy	UTS ksi, min.	0.2% YS ksi, min.	% Elong., min.	% Reduction in Area
K-500	130	85	20	---
Alloy 725	165	120	20	35
Alloy 925	168 TYP	110 TYP	27 TYP	45 TYP
UNS N07716 (625+, 625PH)	165	120	20	35
Alloy 718	185	150	12	15
Rene 41	170	130	8	10
MP35N	260	230	8	35
MP159	260	250	6	22
Ti-6Al-4V, Ti-6Al-4V ELI	115	105	12	20
Ti 38-6-44	120	115	10	25
Ti 5111	126 TYP	111 TYP	13 TYP	29 TYP
Ti 16-2.5-3	130 TYP	120 TYP	20 TYP	---
Alloy A286	130	85	15	18
17-4 PH H1100	140	115	14	35

CORROSION PROPERTIES

Localized Corrosion Resistance

A summary of the maximum calculated pitting and crevice rates for the fastener alloys is provided in Table III.

The nickel-base and stainless fastener alloys including Alloy K-500, Alloy 725, Alloy 925, UNS N07716 (Alloys 625+ and 625PH), Alloy 718, Alloy A286, and 17-4 PH are susceptible to localized corrosion in quiescent and low velocity seawater conditions where adequate aeration is not available to maintain the passive surface film. Crevices formed by deposits such as barnacles or in fastener threads can promote initiation of localized corrosion. Components should be designed to minimize areas where seawater can collect, and a water-displacing lubricant or sealant should be applied to the fastener threads. Cathodic protection appears to be an effective method for minimizing localized corrosion of passive film forming alloys. A corrosion test of Alloy A286 bolts threaded into a titanium plate and immersed in quiescent, natural seawater showed cathodic

protection (zinc or iron anodes) to be effective in preventing localized corrosion of Alloy A286 within the tight crevices formed at the fastener thread-plate interfaces for up to one year

Table III.   Summary of Localized Corrosion Resistance Data in Quiescent and Low Flow Natural Seawater (6 Month to 2 Year Exposure Periods)

Alloy	Max. crevice corrosion rate, metal to metal (mm/yr)	Max. crevice corrosion rate, metal to nonmetal (mm/yr)	Max. pitting corrosion rate (mm/yr)
K-500	0.29-0.72[a] (1, unpublished data)	0.03-0.50[a,b] (2, unpublished data)	0.32-0.51[a,c] (1,3)
Alloy 725	0.10-0.13[d] (unpublished data)	0.36[d] (unpublished data)	no data found
Alloy 925	susceptible (4); rates not available	susceptible[a,b] (5); rates not available	susceptible (4); rates not available
UNS N07716	0.05-0.08[d] (unpublished data)	0.08-0.51[d] (unpublished data)	no data found
Alloy 718	2.09[a] (1)	0.51-0.97[b] (2)	negligible[a,b] (1,6)
Rene 41	immune[b,c] (1,6)	immune[c] (6)	immune[b,c] (1,6)
MP35N	immune[b,f] (7-12)	immune[f] (2)	immune[f] (2,12,13)
MP159	immune (11,12)	no data found	immune (12)
Ti-6Al-4V, TI-6Al-4V ELI	immune[b] (14, unpublished data)	immune[b] (2,14, unpublished data)	immune[c] (3)
Ti 38-6-44	Immune[b] (unpublished data)	immune[b] (unpublished data)	no data found
Ti 5111	no data found	no data found	no data found
Ti 16-2.5-3	no data found	no data found	no data found
Alloy A286	susceptible (10); rates not available	insufficient data	susceptible (10); rates not available
17-4 PH	susceptible (10); rates not available	no data found	0.98-1.70[c] (3)

[a]: annealed and aged
[b]: annealed
[c]: wrought
[d]: ST and dual-aged
[e]: annealed and overaged
[f]: cold worked (50% or more)

Both Rene 41 and MP35N are highly resistant to localized corrosion in quiescent and low velocity seawater. Localized corrosion data for MP159 in seawater are scant, but limited data from a one-year seawater immersion test showed the material to be resistant to crevice corrosion. Ti-6Al-4V (ELI) and Ti 38-6-44 are also highly resistant to localized corrosion in low and high velocity seawater as well as marine atmospheric, splash/spray, and tidal environments at ambient temperature. No localized corrosion information was found for Ti 5111 or Ti 16-2.5-3 alloys in ambient temperature seawater. These titanium alloys would be expected to have good localized

corrosion resistance in this environment, since titanium alloys generally exhibit localized attack only within tight crevices while immersed in hot (>160°F) chloride solutions (15).

The crevice corrosion resistance of Alloy K-500, Alloy 725, Alloy 925, UNS N07716 (625+, 625PH), Alloy 718, Alloy A286, and 17-4 PH is considered to be unacceptable for fasteners exposed to the marine environments of interest unless adequately protected. Rene 41, MP35N, Ti-6Al-4V (ELI), and Ti 38-6-44 are immune to both crevice corrosion and pitting in marine environments and are acceptable fastener candidates, based on localized corrosion data. MP159, Ti 5111 and Ti 16-2.5-3 alloys are also expected to be suitable fastener alloys in terms of localized corrosion resistance.

Compatibility (Galvanic and/or Crevice Corrosion)

The relative compatibility, based on galvanic and crevice corrosion behavior, of the fastener alloys under consideration is summarized in Table IV. The compatibility of the candidate fastener alloys with Alloy 625, a nickel-base, marine structural alloy, is of particular interest for naval applications and is included whenever data are available.

Table IV. Summary of Compatibility (Galvanic and/or Crevice Corrosion) in Marine Environments

Candidate Alloy	Dissimilar Alloy	Relative Compatibility[a] (Galvanic and/or Crevice Corrosion) of Candidate and Dissimilar Alloys	References
K-500	Alloy 625	Poor; severe galvanic corrosion of K-500, especially for high 625:K-500 surface area ratios; anodic to 625	3,16,17, unpublished data
K-500	Ti-6211	Poor; general and localized corrosion rates of K-500 are galvanically increased, especially for high Ti-6211:K-500 area ratios	
Alloy 725	Alloy 625	Good; little to no corrosion, Alloy 725 remains slightly cathodic to Alloy 625	16, unpublished data
Alloy 925	Alloy 625	Poor; galvanically compatible, but severe crevice corrosion of Alloy 925 unless cathodically protected	4,5
UNS N07716 (625+, 625PH)	Alloy 625	Marginal; little to no corrosion, but potential of UNS N07716 may fluctuate and remain anodic to 625	unpublished data
Rene 41		No data found	

[a]Good indicates no significant corrosion of either the candidate or dissimilar alloy.
Marginal indicates slight to moderate galvanic or crevice corrosion of one or both alloys.
Poor indicates severe galvanic or crevice corrosion of one or both alloys.

Table IV. (continued)

Candidate Alloy	Dissimilar Alloy	Relative Compatibility[a] (Galvanic and/or Crevice Corrosion) of Candidate and Dissimilar Alloys	References
Alloy 718	aluminum alloys	Marginal; slight to moderate galvanic corrosion of the aluminum alloys; Alloy 718 compatibility with aluminum alloys > Alloy A286 but < Ti-6Al-4V	18,19
Alloy 718	Alloy 625	Poor; corrosion potential data suggest galvanic compatibility, but severe localized corrosion of Alloy 718 possible unless cathodically protected	
MP35N	Alloy K-500	Poor; galvanic corrosion of K-500	7,10,11,18, 20
MP35N	316 stainless	Poor; galvanic corrosion of 316	
MP35N	carbon steel	Poor; galvanic corrosion of carbon steel	
MP35N	7075-T6 Al, 5456 Al	Poor; galvanic corrosion of aluminum alloys	
MP35N	17-4 PH	Poor; although little galvanic corrosion, severe 17-4 PH crevice corrosion	
MP35N	HY-130	Good; slight corrosion of HY-130, but no increase due to galvanic coupling	
MP35N	Ti-6Al-4V	Good; no corrosion	
MP35N	Alloy 625	Good; no corrosion	
MP159	Alloy 625	Good; no corrosion	11
MP159	Alloy K-500	Poor; galvanic and crevice corrosion of K-500	
MP159	Alloy 718	Poor; crevice corrosion of Alloy 718	
Ti 38-6-44	Alloy 625	Good; no galvanic corrosion, Ti-38-6-44 slightly cathodic to Alloy 625; crevice corrosion of Alloy 625 possible unless cathodically protected	unpublished data

[a]Good indicates no significant corrosion of either the candidate or dissimilar alloy.
Marginal indicates slight to moderate galvanic or crevice corrosion of one or both alloys.
Poor indicates severe galvanic or crevice corrosion of one or both alloys.

Table IV. (continued)

Candidate Alloy	Dissimilar Alloy	Relative Compatibility[a] (Galvanic and/or Crevice Corrosion) of Candidate and Dissimilar Alloys	References
Ti-6Al-4V ELI	Alloy 625	Good; no galvanic corrosion, Ti-6Al-4V slightly cathodic to Alloy 625; crevice corrosion of Alloy 625 possible unless cathodically protected	3,10,14,18, 21, unpublished data
Ti-6Al-4V	aluminum alloys	Marginal to Poor; no corrosion of Ti-6Al-4V, but mild to severe galvanic corrosion of aluminum alloys	
Ti-6Al-4V	titanium alloys	Good; no corrosion	
Ti-6Al-4V	stainless steel A286, 17-4 PH	Poor; no corrosion of Ti-6Al-4V, but severe crevice corrosion of Alloy A286 and 17-4 PH	
Ti-6Al-4V	steel, iron	Good; mild corrosion of HY-130, but no increase in rate due to galvanic coupling	
Ti-6Al-4V	zinc	Good; no corrosion	
Ti-6Al-4V	fiberglass	Good; no corrosion	
Ti 5111		No data found but expected to be similar to Ti-6Al-4V	
Ti 16-2.5-3		No data found but expected to be similar to Ti-6Al-4V	
Alloy A286	aluminum alloys	Marginal; moderate corrosion of aluminum alloys (Alloy A286 less compatible than Alloy 718 or Ti-6Al-4V with aluminum alloys)	10,18,22,23
Alloy A286	17-4 PH	Poor; little galvanic corrosion, but severe crevice corrosion of 17-4 PH possible	
Alloy A286	HY-130	Good; no increased corrosion of HY-130 due to galvanic coupling	
Alloy A286	Ti-6Al-4V	Poor; severe crevice corrosion of Alloy A286	

[a]Good indicates no significant corrosion of either the candidate or dissimilar alloy.
Marginal indicates slight to moderate galvanic or crevice corrosion of one or both alloys.
Poor indicates severe galvanic or crevice corrosion of one or both alloys

Table IV. (continued)

Candidate Alloy	Dissimilar Alloy	Relative Compatibility* (Galvanic and/or Crevice Corrosion) of Candidate and Dissimilar Alloys	References
17-4 PH	2024-T4 Al	Poor; galvanic corrosion of 2024-T4	3,10
17-4 PH	anodized steel	Poor; galvanic corrosion of anodized steel	
17-4 PH	304 stainless	Poor; increased crevice corrosion of 304 stainless	
17-4 PH	Ti 6211	Poor; increased 17-4 PH corrosion	

*Good indicates no significant corrosion of either the candidate or dissimilar alloy.
Marginal indicates slight to moderate galvanic or crevice corrosion of one or both alloys.
Poor indicates severe galvanic or crevice corrosion of one or both alloys

Nickel-Base Alloys—Alloy K-500 was found to be galvanically incompatible with Alloy 625, and the extent of galvanic corrosion of Alloy K-500 increased substantially as the relative surface area of Alloy 625 was increased. Testing of K-500 coupled to Ti 6211 also showed K-500 to be galvanically incompatible with the Ti alloy as evidenced by increased general corrosion and crevice corrosion rates of K-500. The extent of corrosion of K-500 became more severe as the surface area ratio of Ti 6211:K-500 was increased. Galvanic corrosion testing has shown Alloy 725 to be highly compatible with Alloy 625, with Alloy 725 cathodic to Alloy 625. It is recommended that Alloy 925:Alloy 625 couples only be utilized with corrosion control. Although the two alloys are galvanically compatible, severe crevice corrosion of Alloy 925 may occur unless adequate protection is provided. The compatibility of UNS N07716 (625+, 625PH) with Alloy 625 is considered marginal. In galvanic corrosion testing, the UNS N07716 was found to fluctuate from anodic to cathodic polarization with respect to Alloy 625 during the six month test period. Galvanic testing of Alloy 718 with various aluminum alloys showed marginal compatibility. The aluminum alloys exhibited slight to moderate galvanic corrosion. Alloy 718 compatibility with the aluminum alloys was judged to be better than that of Alloy A286 but less than that of Ti-6Al-4V with the same group of aluminum alloys. It is recommended that Alloy 718 not be used with Alloy 625 without corrosion control. Although the corrosion potentials of these alloys are similar and thus have good galvanic compatibility, severe localized corrosion of Alloy 718 will occur unless adequate protection is provided.

The highly cathodic Multiphase alloys did not corrode in any of the galvanic couples tested and reported. MP35N showed poor galvanic compatibility with Alloy K-500, 316 stainless, carbon steel, 7075-T6 Al, and 5456 Al. Coupling MP35N with these more anodic alloys causes their corrosion rates to be increased. Stainless steel 17-4 PH is more galvanically compatible with MP35N than the previously listed alloys, but the 17-4 PH is susceptible to severe

localized corrosion without protection. MP35N is compatible with Alloy 625, HY-130, and Ti-6Al-4V; none of these alloys showed increased corrosion rates when coupled with MP35N. MP159 showed poor compatibility with Alloys K-500 and 718. Coupling MP159 to Alloy K-500 leads to galvanic and crevice corrosion of the K-500. Coupling MP159 with Alloy 718 does not cause galvanic corrosion of either alloy, but it does result in crevice corrosion of the 718. MP159 is compatible with Alloy 625.

Titanium-Base Alloys— As expected, the highly cathodic titanium alloys did not corrode in any of the galvanic couples tested and reported. Galvanic corrosion testing of Ti-6Al-4V (ELI) with various materials including Alloy 625, titanium alloys, steel, iron, zinc, and fiberglass showed good compatibility in all cases. Coupling Ti-6Al-4V to Alloy A286 and to 17-4 PH, however, led to severe crevice corrosion of both of the stainless alloys. The galvanic compatibility of Ti-6Al-4V with aluminum alloys was judged marginal to poor due to mild to severe corrosion of the aluminum alloys. Ti 38-6-44 was found to be compatible with Alloy 625. No galvanic corrosion data were found for Ti 5111 or Ti 16-2.5-3, but it would be expected that these alloys would have similar compatibility as was found for Ti-6Al-4V (ELI).

Stainless Alloys—The compatibility of Alloy A286 with aluminum alloys was considered marginal due to moderate galvanic corrosion present on some of the aluminum alloy samples; overall, Alloy A286 was less compatible with aluminum alloys than either Alloy 718 or Ti 6Al-4V. Coupling Alloy A286 with either 17-4 PH or with Ti-6Al-4V is not recommended. The Alloy A286:17-4 PH couple resulted in minimal galvanic corrosion but severe localized corrosion of the 17-4 PH. The Alloy A286:Ti-6Al-4V coupling resulted in intense crevice corrosion and pitting observed on the Alloy A286 fasteners, which may have been enhanced by anodic polarization resulting from galvanic coupling to Ti-6Al-4V. The Alloy A286: HY-130 couple exhibited good galvanic compatibility, with no notable increase in the general corrosion of the HY-130 panels.

Alloy 17-4 PH is not recommended for use with 2024-T4 Al, anodized steel, 304 stainless, or Ti 6211. Anodized steel and 2024-T4 Al have shown galvanic corrosion when coupled with 17-4 PH. Increased crevice corrosion was observed on 304 stainless coupled with 17-4 PH. The Ti 6211:17-4 PH couple resulted in increased crevice corrosion and galvanic corrosion of the 17-4 PH.

Methods to Control Galvanic Corrosion

Galvanic corrosion of fasteners exposed to marine environments can be minimized by following several general guidelines. First, when selecting a fastener alloy to join a dissimilar metal or alloy, the alloy selected for the fastener should be more noble (more cathodic) than the joint material(s). Use of a fastener that is cathodic to the joint material avoids unfavorable surface area ratios and minimizes galvanic corrosion of the fastener. The galvanic series in seawater (16) is useful for selecting a fastener material that is cathodic to the component material of interest. In some cases where fastener materials more anodic than the joint material have been used, external sources of cathodic protection such as anodes or impressed current have been relied upon to

protect the fasteners from corrosion. It should be noted that electrical continuity is necessary to ensure cathodic protection of the fastener; the presence of dielectric films or coatings on the fastener or joint material may result in electrical isolation of the fastener. It is for this reason that fastener materials should also have inherently good general and localized corrosion resistance.

Second, fastener materials should be selected based on demonstrated galvanic compatibility with the joint material. As previously discussed, the galvanic series can be used to determine the anodic and cathodic member of the galvanic couple but has been shown to be a poor indicator of the extent or rate of corrosion (18). Galvanic corrosion has been observed on alloys with as little as 100 mV difference in potential. Experimental data, such as galvanic current measurements or weight loss measurements, are needed to accurately predict galvanic corrosion rates.

Third, to further minimize galvanic corrosion, the dissimilar metals may be electrically isolated. Nonmetallic sleeves and washers can be used in through-hole fastening systems to isolate the fastener from the joint material. A dielectric lubricant or antiseize may be applied to the fastener to isolate it from a joint material or nut, but complete coverage of the lubricant on the fastener is difficult to assure, especially when high installation torques are applied. Even dry film lubricants can be difficult to maintain on fastener threads subjected to repeated "make/break" cycles. Experimental evaluation of such products as galvanic insulators should be performed prior to their use in the field.

Environmentally Assisted Cracking (EAC) and Sustained Load Cracking (SLC) Resistance

The susceptibility of the high strength fastener alloys under consideration to EAC and SLC is summarized in Table V. The supporting data summarized in Table V are for the condition of interest for each material except as noted.

Table V. Summary of EAC and SLC Resistance in Seawater

Alloy and Condition	EAC and SLC Susceptibility	Supporting Data[a]	References
Alloy K-500 (Solution treated and aged)	Susceptible to HE (at or electronegative to -850 mV$_{SCE}$); resistant to SLC at service temperatures of interest	Slow strain rate (A, FC, CP); fracture toughness, J$_{Ic}$ (A, CP); U-bends (FC, 2 yr.); proving rings w/notched bars stressed to 90% of 0.2% YS (FC, CP, 7 mo.); failure analyses	1,24-31
Alloy 725 (Solution treated and dual aged)	Susceptible to SCC and to HE (at or electronegative to -850 mV$_{SCE}$); SLC unknown	Slow strain rate (A, FC, CP); threaded rod in bending (FC, CP, 1.2 yr.)	unpublished data

Table V. (continued)

Alloy and Condition	EAC and SLC Susceptibility	Supporting Data[a]	References
Alloy 925 (Solution treated and dual aged)	Susceptible to HE at -1250 mV$_{SCE}$; reduced load bearing capacity evident in air, freely corroding, -850, and -1000 mV$_{SCE}$ conditions; SLC unknown	Slow strain rate (A, FC, CP)	28
UNS N07716 (Solution treated and dual aged)	Resistant to SCC; susceptible to HE (at or electronegative to -850 mV$_{SCE}$); SLC unknown	Slow strain rate (A, FC, CP); proving rings with notched bars stressed to 90% of 0.2% YS (FC, CP, 7 mo.); threaded rod in bending (FC, CP, 1.2 yr.)	28,29, unpublished data
Alloy 718 (Solution treated and dual aged)	Resistant to SCC; susceptible to HE (at or electronegative to -850 mV$_{SCE}$); SLC unknown	Slow strain rate (FC, CP, A); U-bends (FC, 2 yr.); fracture toughness, K$_{Ith}$ (A, FC, CP, tested in acidic chloride solutions)	1,32,33, unpublished data
Rene 41 (Solution treated and aged)	Resistant to SCC; susceptible to HE at or electronegative to -1000 mV$_{SCE}$; SLC unknown	Slow strain rate (A, FC, CP); U-bends (FC, 2 yr.)	1,28
MP35N (Solution treated, cold worked and aged)	Resistant to HE and SCC; SLC unknown	C-rings (FC, 6 mo.), tensile specimens (FC, 6 mo.) and bolts (galvanically coupled, 41 days to 7 mo.) stressed to varying levels of 0.2% YS or UTS and alternately immersed; fracture toughness, K$_{Ith}$ (A, FC, CP)	12,34-36
MP159 (Solution treated, cold worked and aged)	Limited data suggest resistance to HE and SCC; SLC unknown	Bolts stressed to 75% of UTS and alternately immersed (galvanically coupled, 41 days to 7 mo.)	12,35
Ti-6Al-4V, Ti-6Al-4V ELI (Solution Treated and	Variable susceptibility to HE and SCC (dependent on composition, microstructure); lower oxygen of ELI grade improves EAC resistance; susceptible to SLC	Slow strain rate (A, FC, CP); fracture toughness, K$_{Ith}$ (A, FC, CP); proving rings with notched bars stressed to 90% of 0.2% YS (FC, CP, 7 mo.);	28-30,37-53

Annealed)	(based on plate data)	U-bends (FC, 20 days to 1.8 yr.)	

*A=*air* tested; FC=tested *freely corroding* in seawater (SW) or 3.5% NaCl; CP=tested under *cathodic polarization* in SW or 3.5% NaCl

Table V. (continued)

Alloy and Condition	EAC and SLC Susceptibility	Supporting Data[a]	References
Ti 38-6-44 (Solution Treated and Annealed)	Resistant to HE and SCC; SLC unknown	Slow strain rate (A, FC, CP); fracture toughness, K_{Ith} (A, FC, CP); proving rings with notched bars stressed to 90% of 0.2% YS (FC, CP, 7 mo.)	28-30,32, 54-58
Ti 5111 (As-forged)	Resistant to HE and SCC; SLC unknown	Slow strain rate (A, FC, CP); fracture toughness, K_Q (A, FC)	30, unpublished data
Ti 16-2.5-3 (Solution Treated and Overaged)	Resistant to HE and SCC; SLC unknown	Slow strain rate (A, FC, CP); fasteners of *ST and aged material*, stressed to 75-105% of 0.2% proof stress (CP, 2 mo. to 2 yr.); U-bends of *ST and aged material*, stressed to 55% of 0.2% YS and alternately immersed (FC, 2 mo.)	29,30,59,60
Alloy A286 (Solution Treated and Aged)	Resistant to HE and SCC; SLC unknown	Slow strain rate (A, FC, CP); C-ring and tensile specimens of *cold worked and aged material* stressed to 75-100% of 0.2% YS (FC, 6 mo.); fracture toughness, K_{Ith} (A, FC)	28,32,36,61
17-4 PH (Solution Treated and Aged)	HE and SCC resistance increases as tempering temperature increases from 900 to 1100°F; at higher tempering temperatures (1050°F), a -600 to -1300 mV_{SCE} potential required for protection; SLC unknown	Bent beams stressed to 90% of 0.2% YS (FC, CP); fracture toughness, K_{Ith} (A, FC, CP)	62-64

[a]A=*air* tested; FC=tested *freely corroding* in seawater (SW) or 3.5% NaCl; CP=tested under *cathodic polarization* in SW or 3.5% NaCl

Nickel-base Alloys—The susceptibility of Alloy K-500 to HE has been well-documented in the literature. The susceptibility threshold lies between -670 and -850 mV_{SCE}. Based on the limited data available for Alloy 725, UNS N07716 (Alloy 625+, 625PH), and Alloy 718 in the solution treated and dual aged condition, these Ni-Cr-Mo alloys offer little improvement over K-500. Rene 41, in the solution treated and aged condition, has shown a slight improvement in HE resistance over Alloy K-500. The slow strain rate test data for Rene 41 indicate resistance to HE

at -850 mV$_{SCE}$ and susceptibility at -1000 mV$_{SCE}$. Slow strain rate testing of Alloy 925 showed a HE susceptibility at -1250 mV$_{SCE}$ and a ductile intergranular fracture mode in air, freely corroding, -850 mV, and -1000 mV$_{SCE}$ environments. This intergranular fracture mode is indicative of a reduced load bearing capacity for this alloy, but the extent of the load reduction in service is not known. MP35N was the only nickel-base alloy with demonstrated HE and SCC resistance. Very limited data suggest similarly high HE and SCC resistance for MP159 in the cold-worked and aged condition.

SLC has not been detected in properly processed Alloy K-500 subjected to ambient temperatures. No data were available on the remaining nickel-base alloys; however, they are expected to exhibit a SLC resistance similar to K-500.

Titanium-base Alloys—Ti 38-6-44 has been shown to have good resistance to EAC in seawater in the solution annealed condition, which is the condition of interest for naval fastener applications. Ti 5111 (α-β forged) and Ti 16-2.5-3 (solution treated and overaged) also demonstrated good EAC resistance in chloride conditions. Annealed Ti-6Al-4V has been shown to have variable resistance to EAC, dependent on the composition and microstructure of the material, as well as the configuration and size of the specimen. The ELI grade, with less than 1200 ppm oxygen, has slightly improved resistance over higher-oxygen content specimens.

Testing of Ti-6Al-4V plate has shown this alloy to be susceptible to SLC under certain conditions. Some researchers have found interstitial content to play a key role in determining SLC susceptibility, while others have found no dependence of SLC on composition or processing. Texture has been found to markedly affect SLC of Ti-6Al-4V plate. Based on data obtained from plate, it can be said that Ti-6Al-4V bar stock may show degradation in fracture resistance under sustained loading conditions; relative degradation due to SLC may be assumed to be similar to that observed in plate. SLC testing of bar material in the condition of interest is needed to confirm these assumptions. Lack of sufficient data on SLC of Ti 38-6-44, Ti 5111, and Ti 16-2.5-3 also make predictions of SLC resistance equally difficult.

Stainless Alloys—Alloy A286 has shown good EAC resistance based on laboratory slow strain rate testing. A286 specimens were evaluated in both freely corroding seawater and in cathodically polarized conditions, where the potential was varied from -850 to -1250 mV$_{SCE}$. Alloy 17-4 PH is susceptible to EAC; however, the EAC resistance of this alloy significantly increases as the tempering temperature increases from 900 to 1100°F. At higher tempering temperatures (1050°F), limited data (64) suggest that a -600 to -1300 mV$_{SCE}$ potential is required for protection of this alloy from the effects of EAC and localized corrosion. No information was found in the literature regarding the SLC resistance of Alloy A286 or 17-4 PH.

DISCUSSION

In addition to corrosion properties for these high strength fastener alloys, other properties must be considered. Issues specific to the successful use of a particular alloy will be briefly discussed. The high strength properties of MP35N are achieved by cold working this material.

This, however, limits the finished fastener sizes that are capable of being produced. The size limitations result from the manufacturer's inability to cold work large diameter material or the inability to retain the cold work during hot forging of the bolt heads and nuts (65).

For all of the titanium alloys, room temperature creep and galling are of concern. Room temperature creep can occur at applied stresses ranging from 60% σ_y, up to the alloy's proportional limit. Limited data have suggested that a double fastener tightening procedure may be effective in preventing room temperature creep (66, unpublished data). Effective use of titanium alloys as fasteners will require anti-galling surface treatments, and specific treatments should be evaluated in the service environment to assess any adverse corrosion behavior due to the application of these products.

SUMMARY AND CONCLUSIONS

When assessing the corrosion resistance of an alloy, one must consider all forms of corrosion applicable to the end item and its expected service environment. In this paper, the localized and galvanic corrosion and environmentally assisted cracking susceptibilities of 15 fastener alloys have been evaluated for applicability as a fastener alloy in seawater. Obviously, when selecting an alloy for a high-strength fastener application, corrosion resistance is only one consideration; other material properties, such as mechanical and physical properties must also be considered.

Based solely on corrosion resistance, the data reviewed in this paper indicate that MP35N, MP159, Alloy A286, Ti-6Al-4V, Ti 38-6-44, Ti 5111, and Ti 16-2.5-3 are the most promising candidates for high strength fastener applications. MP35N has excellent localized corrosion and EAC resistance. While MP35N is resistant to galvanic attack when coupled with more anodic materials, attack of the more anodic material may be a problem. MP35N is compatible with HY-130 and Ti-6Al-4V, but may require a corrosion control method such as electrical isolation if used with Alloy K-500, steel, stainless steel, or aluminum alloys. For these galvanic couples, however, a small cathode (MP35N fastener) to large anode (joint material) area ratio will lessen the extent of corrosion occurring. Since the high strength of the MP35N alloy is achieved through cold working, there are size limitations for producing MP35N fasteners. This is due to the inability of a) cold working large diameter material or b) retaining the cold work during hot forging of the bolt heads and nuts.

MP159 is also recommended for high strength fastener applications, based on limited seawater corrosion data and expected similarities to MP35N. Limited data suggest high resistance of MP159 to localized corrosion and EAC. MP159, like MP35N, is resistant to galvanic attack when coupled with more anodic materials, but galvanic or crevice attack of the more anodic material may occur. MP159 has been shown to be compatible with Alloy 625. A corrosion control method may be necessary when using an MP159 fastener with an incompatible joint material such as Alloy K-500 or Alloy 718. Like MP35N, strengthening of MP159 is achieved through a combination of cold working and heat treating. MP159, however, is substantially more heat treatable than MP35N, making fastener size limitations less of a concern

for MP159. Furthermore, a 'modified,' lower-strength (150 ksi YS) version of MP159 is currently under development. The 'modified' material condition is expected to show improved fracture properties and improved EAC resistance.

Alloy A286 is also recommended for high strength fastener use due to its excellent EAC resistance. This alloy is susceptible to localized corrosion, though, and would require cathodic protection for effective application in seawater.

Ti-6Al-4V and Ti 38-6-44 are essentially immune to localized corrosion, and Ti-6Al-4V is compatible with Alloy 625, other titanium alloys, steel, iron, zinc, and fiberglass. Coupling Ti-6Al-4V with aluminum alloys may necessitate the use of a corrosion control method to prevent galvanic corrosion of the aluminum. Use of Alloy A286 or 17-4 PH with Ti-6Al-4V would require cathodic protection to prevent crevice corrosion of the stainless alloys. Ti 38-6-44 has shown good galvanic compatibility with Alloy 625. No other galvanic corrosion data were found for Ti 38-6-44, although this material should have a galvanic corrosion resistance similar to Ti-6Al-4V. Ti 38-6-44 in the solution annealed condition is resistant to hydrogen embrittlement and stress corrosion cracking. The resistance of Ti-6Al-4V to stress corrosion cracking has been found to vary, depending on the composition and processing of the material as well as the size and configuration of the specimen or end item. The low-oxygen ELI grade of Ti-6Al-4V has been found to generally improve the alloy's resistance to stress corrosion cracking. Ti-6Al-4V has also exhibited a susceptibility to SLC based on plate data only. Both Ti 5111 and Ti-16-2.5-3 have good EAC resistance in seawater environments. No seawater localized corrosion or galvanic compatibility data were found in the literature for these alloys, but they would be expected to have corrosion properties similar to Ti-6Al-4V.

Other concerns with effectively using titanium alloys as fastener materials include room temperature creep and galling. High strength titanium alloys are susceptible to room temperature creep at applied stresses varying from 60% σ_{ys} up to the alloy's proportional limit. A double fastener tightening procedure may be effective in eliminating room temperature creep in fastened joints. Anti-galling surface treatments are available for titanium alloys, but specific treatments should first be evaluated in the service environment that the fastener would be used since the use of such products can affect the corrosion behavior of the system.

REFERENCES

1. Niederberger, R.B., R.J. Ferrara, and F.A. Plummer, "Corrosion of Nickel Alloys in Quiet and Low Velocity Sea Water," *Materials Protection and Performance*, Vol. 9, No. 8, 1970, pp. 18-22.

2. Lennox, T.J., Jr., M.H. Peterson, and C.W. Billow, "Corrosion Resistance and Response to Cathodic Protection of Advanced Alloys in Seawater," *Materials Performance*, June 1983, pp. 49-55.

3. Caplan, I.L. and H.P. Hack, "The Galvanic Effects of Titanium Coupled to Various Marine Alloys in Seawater", DTNSRDC/SME-80/54, Oct. 1980.

4. Kain, R.M., "Galvanic/Crevice Corrosion Resistance of Directly Coupled Incoloy alloy 925 and Inconel alloy 625 in Seawater: 6-Month Status Report," LaQue Center for Corrosion Technology, Inc. report for Inco Alloys International, Inc., September 1995.

5. Kain, R.M., "Galvanic Corrosion Testing of Inconel alloy 625 and Incoloy alloy 925 in Ambient Temperature Seawater," LaQue Center for Corrosion Technology, Inc. report for Inco Alloys International, Inc., January 1995.

6. Hack, H.P., "Mechanical, Corrosion, and Fatigue Properties of 15-5 PH, Inconel 718, and Rene 41 Weldments," NSRDC, Report 4528, May 1975.

7. Taylor, E., "Corrosion Resistance of Multiphase Alloys," *Materials Protection*, Vol. 9, No. 3, March 1970, p. 29-31.

8. Multiphase MP35N Alloy Technical Data, Latrobe Steel Company, 1994 revision.

9. Teel, R.B., "Performance of MP35N Ni-Co-Cr-Mo Wire Strand and Wire Rope in Marine Environments, " International Nickel Company Internal Report - Reference Nos. FLL2150.1, HIP 44544 and 4544A, December 27, 1972.

10. Hack, H.P., "Seawater Corrosion of Fasteners in Various Structural Materials," DTNSRDC Report #76-0034, April 1976 (same as 13)

11. Taylor. E., "Corrosion Characteristics of Similar and Dissimilar Metal Couples in Flowing Seawater," SPS Report No. 6004, January 16, 1979.

12. Taylor, E. "A Summary of Aerospace Bolting Alloy Evaluations by Three Different Stress Corrosion Cracking Resistance Test Methods," SPS Report No. 5752, September 3, 1975.

13. Uhlig, H.H. and A.I. Asphahani, "Corrosion Behavior of Cobalt Base Alloys in Aqueous Media," *Materials Performance*, Vol. 18, No. 11, November 1979, pp. 9-20.

14. Thomas, D.E., "Analysis of Cathodically Protected Ti-6Al-4V," R&D Tech Brief 87-3, RMI, February 1987.

15. *Metals Handbook Vol. 13, Corrosion*, ASM International, Metals Park, Ohio, 1987.

16. Hibner, E.L. and R.H. Moeller, "Corrosion-Resistant Alloys UNS N09925 and N07725 for Oilfield Applications," OTC 7206, presented at the 25th Annual Offshore Technology Conference, Houston, TX, May 1993.

17. Thomas, E.D., E.A. Hogan, and K.E. Lucas, "Fasteners in Marine Service," Offshore Technology Conference, OTC 6585, 1991.

18. Mansfeld, F., D.H. Hengstenberg, and J.V. Kenkel, " Galvanic Corrosion of Al Alloys; I. Effect of Dissimilar Metals," *Corrosion*, Vol. 30, No. 10, Oct. 1974, pp.343-353.

19. Private communication with R.M. Kain of LaQue Center for Corrosion Technology, Wrightsville Beach, NC, 4 June 1996.

20. Taylor, E., "Galvanic Compatibility of Coated and Bare MP35N Bolts with 6Al-4V Ti, 7075-T6 Al and Cadmium Plated Steel Structures," SPS Steel Structures," SPS Report No. 5302 Revised, September 15, 1971.

21. "SRB Materials and Processes Assessment from Laboratory and Ocean Environmental Tests," NASA TM-78187, George C. Marshall Space Flight Center, Alabama, June 1978.

22. Thompson, S.D., B.L. White, and J.A. Snide, "Accelerated Corrosion Testing of Graphite/Epoxy Composites and Aluminum Alloy Mechanically Fastened Joints," AFWAL-TR-84-3115, June 1985.

23. Taylor, E., "Fastener Corrosion in Hydrospace," NACE Corrosion '74, Paper #79, Houston, TX, March 1974.

24. Joosten, M.W. and L.H. Wolfe, "Failures of Nickel-Copper Bolts in Subsea Applications," Offshore Technology Conference, OTC 5553, Houston, TX, April 1987.

25. Efird, K.D., "Failure of Monel Ni-Cu-Al Alloy K-500 Bolts in Seawater," *Materials Performance*, Vol. 24, No. 4, April 1985, pp. 37-40.

26. Harris, J.A., R.C. Scarberry, and C.D. Stephens, "Effects of Hydrogen on the Engineering Properties of MONEL Nickel-Copper Alloy K-500," *Corrosion*, Vol. 28, No. 2, February 1972, pp. 57-62.

27. Harris, J.A. and E.F. Clatworthy, "Hydrogen Embrittlement of Incoloy alloy 925, Monel alloy K-500, and Inconel alloy 625 by Slow Strain Rate Method," NACE Corrosion '86, Paper #150, Houston, TX, March 1986.

28. Aylor, D.M. "High Strength Alloys for Seawater Fastener Applications," Proceedings of the Tri-Service Corrosion Conference, Orlando, Florida, June 1994.

29. Aylor, D.M., "An Environmental Cracking Evaluation of Fastener Materials for Seawater Applications," NACE Corrosion '94, Paper #484, 1994.

30. Tregoning, R.L., D.M. Aylor, and I.L. Caplan, "High Strength Titanium Alloys for Naval Fastener Applications," Proceedings of the 8th World Conference on Titanium, Birmingham, England, October 1995.

31. Vassilaros, M. J., et al., "Environmental Slow Strain Rate J-Integral Testing of K-500," ASTM STP 1210, *Slow Strain Rate Testing for the Evaluation of Environmentally Induced Cracking*, 1993, pp. 123-133.

32. Wolfe, L.H., C.C. Burnette, and M.W. Joosten, "Hydrogen Embrittlement of Cathodically Protected Subsea Bolting Alloys," *Materials Performance*, Vol. 32, No. 7, July 1993.

33. Lillard, J.A., R.G. Kelly, and R.P. Gangloff, "Effect of Electrode Potential on Stress Corrosion Cracking and Crack Chemistry of a Nickel-Base Superalloy," NACE Corrosion '97, Paper #197, Houston, TX, 1997.

34. Montano, J.W., "A Mechanical Property and Stress Corrosion Evaluation of MP35N Multiphase Alloy," NASA TM X-64591, Marshall Space Flight Center, Alabama, May 1971.

35. Taylor, E., "Multiphase Alloy Environmental Resistance," Standard Pressed Steel, Report No. 5817, Jenkintown, June 1976.

36. Stonesifer, F.R., H.L. Smith, and H.E. Romine, "Evaluation of Three Materials as Candidates for Lift-Pad Studs in an Ocean Environment," NRL Memorandum Report 2068, Naval Research Laboratory, November 1969.

37. Yoder, G.R., C.A. Griffis, T.W. Crooker, "The Cracking of Ti-6Al-4V Alloys Under Sustained Load in Ambient Air," *Journal of Engineering Science and Mechanics*, Trans. ASME, October 1974, pp. 268-274.

38. Venkataraman, G. and A.D. Goolsby, "Hydrogen Embrittlement in Titanium Alloys from Cathodic Polarization in Offshore Environments and Its Mitigation," NACE Corrosion '96, Paper #554, 1996.

39. Schliecher, H. and U. Zwicker, "The Effects of Hydrogen in Titanium Alloys," *Z. Metalkund*, Vol. 47, No. 8, 1956, p. 570.

40. Brown, B.F., "Stress Corrosion Cracking Control Measures: 5. Titanium Alloys," American University Chemistry Department, report submitted to the Office of Naval Research, 1975.

41. Judy, R.W., Jr., and R.J. Goode, "Stress Corrosion Cracking Characteristics of Alloys of Titanium in Salt Water," NRL Report #6564, July 21, 1967.

42. Wald, G.G., "Effect of Heat Treatment on Salt Water Delayed Fracture of Titanium Alloys", presented at the 96th AIME Annual Meeting, Los Angeles, CA, 1967.

43. Beacham, D.C. and Meyn, D.A., "The Effect of Thickness Upon Sustained Load Crack Propagation Characteristics of Titanium Alloys," NRL Report 7449, August 8, 1972.

44. Hack, H.P., "Corrosion Considerations for the Use of Ti-6Al-4V in a Window Clamping System at the National Aquarium in Baltimore," report prepared for the National Aquarium.

45. Gerberich, W.W., et al., "Final Report on Evaluation of Selected Titanium Alloys as a Function of Environment and Heat Treatment," Aerojet-General Corporation Report for Annapolis Division, NSRDC, August 1987.

46. Puzak, P.P., et al., "Metallurgical Characteristics of High Strength Structural Materials: Eleventh Quarterly Report," NRL Report #6513, August 1966.

47. Link, F. and D. Munz, "The Initiation of Stress Corrosion Cracking in Ti-6Al-4V Alloy," *Corrosion Science*, Vol. 13, 1973, pp. 809-811.

48. Meyn, D.A., "Effect of Hydrogen on Fracture and Inert-Environment Sustained Load Cracking Resistance of α-β Ti Alloys," *Metallurgical Transactions*, Vol. 5, Nov. 1974, pp. 2405-2414.

49. Boyer, R.R. and W.F. Spurr, "Characteristics of Sustained-Load Cracking and Hydrogen Effects in Ti-6Al-4V," *Metallurgical Transactions A*, Vol. 9A, Jan. 1978, pp. 22-29.

50. Paton, N.E. and R.A. Spurling in *Metallurgical Transactions A*, Vol. 7A, 1976, p. 1769.

51. Williams, D.N. in *Metallurgical Transactions*, Vol. 5, 1974, p. 2351.

52. Williams, D.N. in *Materials Science and Engineering*, Vol. 18, 1975, p. 149.

53. Meyn, D.A., paper presented at TMS-AIME Fall Meeting in Niagra Falls, New York, September 1976.

54. LRA Labs, Inc., "Evaluation of Structural Properties of Grade 5, Grade 8, and Beta C Fasteners for DDG 51 Mast Bolt Applications," Final Report for NSWC/White Oak, 17 Feb. 1995.

55. Somerday, B.P., J.A. Grandle, and R.P. Gangloff, "Yield Strength and Solution Composition Effects on Aqueous Environmental Cracking of Ti-8V-6Cr-4Zr-4Mo-3Al (Beta C)," Proceeding of the Tri-Service Conference on Corrosion, 1994, pp. 375-392.

56. DeLuccia, J.J., "Electrolytic Hydrogen in Beta Titanium," Naval Air Development Final Report, 10 June 1976.

57. Dudik, A.S., "The Effect of Elevated Hydrogen Levels in the Beta C Titanium Alloy," Dynamet Technical Report, Washington, PA.

58. Gaudett, M.A. and J.R. Scully, "Hydrogen Interactions and Embrittlement in Metastable Beta Ti-3Al-8V-6Cr-4Mo-4Zr," in "Environmentally Assisted Cracking of High Strength Beta Titanium Alloys," Final Report, University of Virginia, Report No. UVA/525461/MSE95/102, November 1994.

59. Bavarian, B. and M. Zamanzadeh, "Corrosion Behavior of Beta-21S Titanium Alloy in Chloride-Containing Environments," NACE Corrosion '93, Paper #284, 1993.

60. Grauman, J.S. and D.K. Peacock, "Performance of a High Strength Beta Ti Alloy Under Tensile Load with Cathodic Charging of Hydrogen," Proceedings of the 8th World Conference on Titanium, Birmingham, England, October 1995.

61. Montano, J.W., "An Evaluation of the Mechanical And Stress Corrosion Properties of Cold Worked A-286 Alloy," NASA TM X-64569, February 12, 1971.

62. Judy, R.W., C.T. Fujii, and R.J. Goode, "Properties of 17-4 PH Steel," Naval Research Laboratory, NRL Report No. 7639, 18 Dec 1973.

63. Carter, C.S., et al., "Stress Corrosion Properties of High Strength Precipitation Hardening Stainless Steels," *Corrosion*, Vol. 27, No. 5, May 1971, pp. 190-197.

64. Vreeland, D.C., "Precipitation Hardening Stainless Steel," *Materials Protection*, Vol. 9, No. 1, January 1970, pp. 32-35.

65. Roach, T.A., "Aerospace High Performance Fasteners Resist Stress Corrosion Cracking," *Materials Performance*, Vol. 23, No. 9, September 1984, pp. 42-45.

66. LRA Laboratories, Inc., "Titanium Beta-C, Annealed Titanium 6Al-4V ELI, and K-Monel Room Temperature Creep Test," LRA Report No. RMI 41111-0820, 10 May 1995.

S -title case !

STRUCTURAL TESTING OF CORRODED OFFSHORE TUBULAR MEMBERS

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ABSTRACT

The results of research related to the behavior of corrosion-damaged tubular brace members and their repair is presented. Investigations were conducted involving both large-scale testing and analytical studies. The effects of the geometry of a corrosion patch were investigated in order to evaluate which geometrical parameters have the most significant affect on residual strength and thereby require more precise measurement in the field for use in strength prediction of corroded members. The analytical studies involved assessing the ability of several different methods of analysis to predict the behavior of damaged and repaired members. These analytical methods included simple engineering calculations and more sophisticated nonlinear finite element analysis. The results of the experimental testing indicated that a significant amount of deterioration in member strength could occur due to corrosion damage. The bond and tensile strength of the grout used in the repair was found not to have an effect on ultimate member strength. The accuracy and reliability of the analytical methods to predict damaged member behavior are illustrated by comparing the measured experimental response with predicted response.

INTRODUCTION

Presently, there are over 3500 major offshore fixed platforms located in U.S. waters. The marine environment exposes these platforms to corrosion, requiring the use of counteractive corrosion measures, such as cathodic protection systems and protective coatings. Despite these measures, there are numerous cases reported of platform members which have suffered corrosion damage (Dunn 1983, Cole et al. 1987). Shown in Fig. 1 is a schematic of a corroded brace member, which had been removed from a Gulf of Mexico platform. A survey of this member by Ostapenko et al. (1993) indicated that the member had significant corrosion, consisting of some uniform, but mostly patch-type corrosion. The latter type of corrosion causes a non-uniform reduction of the cross-section's wall thickness. Testing of this, as well as another similar member resulted in a capacity reduction of 35% and 50%, respectively, compared to a corresponding non-corroded tubular. The loss in capacity is attributed to a premature local buckle that formed in the most severely corroded area of the two specimens.

Improvements in oil recovery methods and economical justifications have resulted in many offshore platforms remaining in service beyond their original design lives. The effect of corrosion damage on the safety of these structures has become a growing concern. Knowledge of the residual
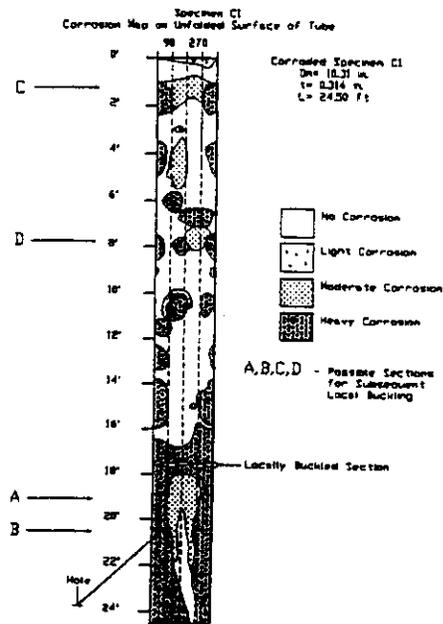
Fig. 1 Corrosion Damage of a Gulf of Mexico Platform Member
[A. Ostapenko et al. 1993]
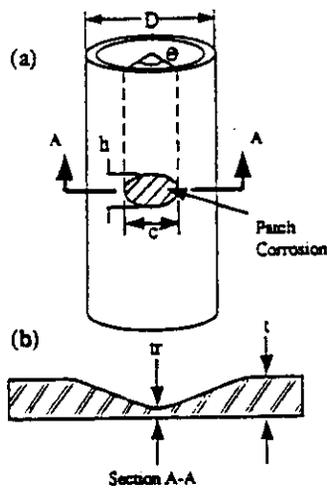
Fig. 2 Geometric Parameters of a Tubular Corrosion Patch
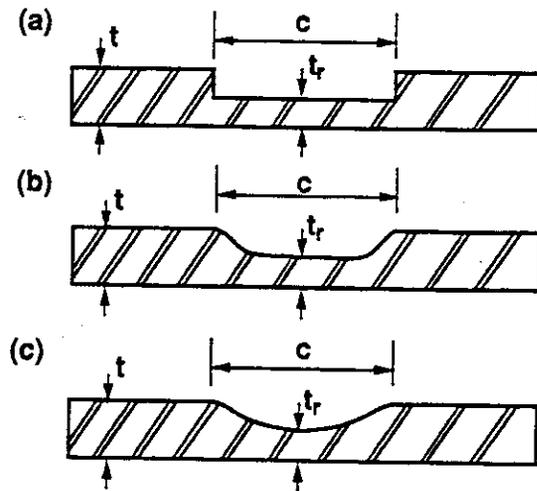
Fig. 3 Corrosion Patch Thickness Profiles Selected for Study: (a) Step, (b) Experimental, and (c) Cosine

strength and reparability of corroded members is highly relevant to the safety, as well as the reparability and requalification of all platforms.

The need to acquire more knowledge about the residual strength and the repair corroded offshore tubular members led to the research report herein. The objectives of these studies (Hebor and Ricles 1994, Paterson 1999) were to investigate the behavior of corroded tubular bracing members in order to assess residual strength, and to evaluate their repair. These studies involved both experimental and analytical investigations, where the former utilized large-scale test specimens. The analytical investigations included performing parametric studies to assess the effects of various geometrical and material properties on member behavior.

RESIDUAL STRENGTH AND REPAIR OF CORRODED TUBULARS

Experimental Program

The experimental study focused on the local buckling strength of corroded tubulars. As noted previously in the study by Ostapenko et al (1993), it was found that the patch with the most severe corrosion controls the local buckling of a tubular member. The study by the authors presented herein involved an investigation into the affects that the geometry of a single patch of corrosion had on the local buckling strength, where the patch was idealized as an ellipse. Cases of multiple patches of corrosion in a cross-section and interaction with long column effects are to be evaluated in future studies. Unlike uniform corrosion, patch type corrosion causes the centroid of the cross-section to shift in a direction away from the patch. This leads to a larger compressive stress to develop at the reduced wall thickness due to the combined effects of compressive axial force and flexure acting on the cross section.

As shown in Fig. 2, the parameters needed to describe the geometry of a corrosion patch include: (1) the length of the major c and minor h axes of the ellipse, where h is equal to the height of the corrosion as measured along the longitudinal axis of the tubular; (2) reduced-to-original wall thickness ratio (t_r/t); and, (3) member diameter-to-thickness ratio D/t. The width of the corrosion patch c is related to the diameter D of the tube and angle θ that it subtends around the circumference, where $c=0.5D\theta$. There are numerous profiles of the wall thickness within the corrosion patch that could be described by the parameters c and t_r/t, as shown in Fig. 3. Measuring accurately the thickness profile of a corrosion patch is difficult in the field due to inspection limitations and adverse environmental conditions. Consequently, the experimental test program involved testing 10 specimens having different sets of values for D/t, t_r/t, and θ, with a thickness profile in the patch that was similar to that shown in Fig. 3(b), which will be referred to as the "experimental" profile. The affect of thickness profile on a member's local buckling strength was assessed analytically by examining a "step" and "cosine" thickness profile shown in Fig. 3(a) and (c), which would represent two extremes. The results from this parametric study will be discussed later.

The matrix of 10 test specimens is shown in Table 1, where D/t ratios of 34, 46, and 64 were investigated. Included in Table 1 are two repaired specimens (Specimens 46-00-95C and 46-00-95E). The nomenclature used to identify each specimen in the test program consisted of

the D/t ratio, t_r/t ratio, and θ, and is included in column 1 of Table 1. Hence, Specimen 34-33-58 was a tubular member having D/t=34, t_r/t = 0.33, and θ = 58 degrees. Specimens 34-100-0, 46-100-0, and 64-100-0 were non-corroded tubulars that were used as control specimens. Specimen 46-00-95 had an elliptical shaped hole, simulating a case of corrosion that had progressed completely through the wall thickness.

Table 1 Corroded Specimen Experimental Test Matrix.

Specimen	D [mm]	t [mm]	t_r/t	θ [deg]	c [mm]	h [mm]	σ_y [MPa]	σ_u [MPa]
34-100-0	218.5	6.4	1.0	0	0	109.5	255.1	400.0
34-33-58	218.4	6.5	0.33	58.4	111.2	109.5	255.1	400.0
34-33-95	218.7	6.5	0.33	95.7	182.6	109.5	255.1	400.0
34-50-311	218.4	6.4	0.51	311	592.8	109.5	255.1	400.0
46-100-0	218.1	4.8	1.0	0	0	109.5	265.5	413.7
46-00-95	218.2	4.8	0.0	95.7	182.1	109.5	265.5	413.7
46-33-95	218.2	4.8	0.36	95.7	182.1	109.5	265.5	413.7
46-67-95	217.9	4.9	0.67	95.7	181.9	109.5	265.5	413.7
64-100-0	218.9	3.4	1.0	0	0	109.5	268.9	420.6
64-60-95	218.9	3.4	0.59	95.7	182.8	109.5	268.9	420.6
46-00-95C*	218.1	4.8	0.0	95.7	182.1	109.5	265.5	413.7
46-00-95E*	218.1	4.8	0.0	95.7	182.1	109.5	265.5	413.7

*Repaired specimen

It was determined from non-linear finite element analysis that the member's local buckling strength was independent of the height h of the patch, as long as h was equal to or greater than $0.5D$. Therefore, in all test specimens, a value of $0.5D$ was used for the height of the corrosion patch. Corroded specimens had a length of L=1409.7 mm and a slenderness ratio of L/r = 18.5. Non-corroded specimens were actually stub columns having a length equal to 3.5 times their diameter. All specimens were fabricated from ERW A53 Type B steel tubulars. For each D/t ratio, specimens were cut from the same tubular.

In order to obtain material properties representative of in-situ offshore tubulars, the steel tubulars with D/t = 34 and 46 were annealed. The average static yield stress σ_y and ultimate stress σ_u are reported in Table 1, and were determined by conducting standard ASTM (1991) tensile coupon tests. The stress-strain relationships determined from the tensile coupon tests of both annealed and non-annealed steel are shown in Fig. 4. The results for σ_y coincided closely with that determined from stub-column tests. The stub-column tests were conducted in accordance with standard procedures (Galambos 1988). Stub-column stress-strain curves indicated that the annealed tubulars had virtually no residual stresses. The specimens fabricated from the tubulars of D/t=64 were found to have a linear stress-strain curve up to at least 90% of the compressive yield stress, indicating that there were no significant residual stresses present in these specimens. Hence, the experimental results reported herein do not include the effects of fabrication residual stresses. However, an analytical study of residual stresses (Hebor and Ricles
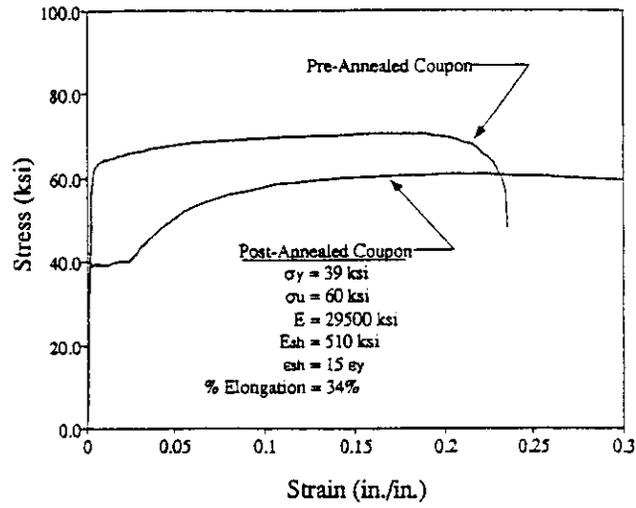
Fig. 4 Typical Stress-Strain Relationship of Annealed ("Post-Annealed") and Non-annealed ("Pre-Annealed") Steel, D/t = 46. [Note: 1 ksi = 6.896 MPa]


(a)

(b)
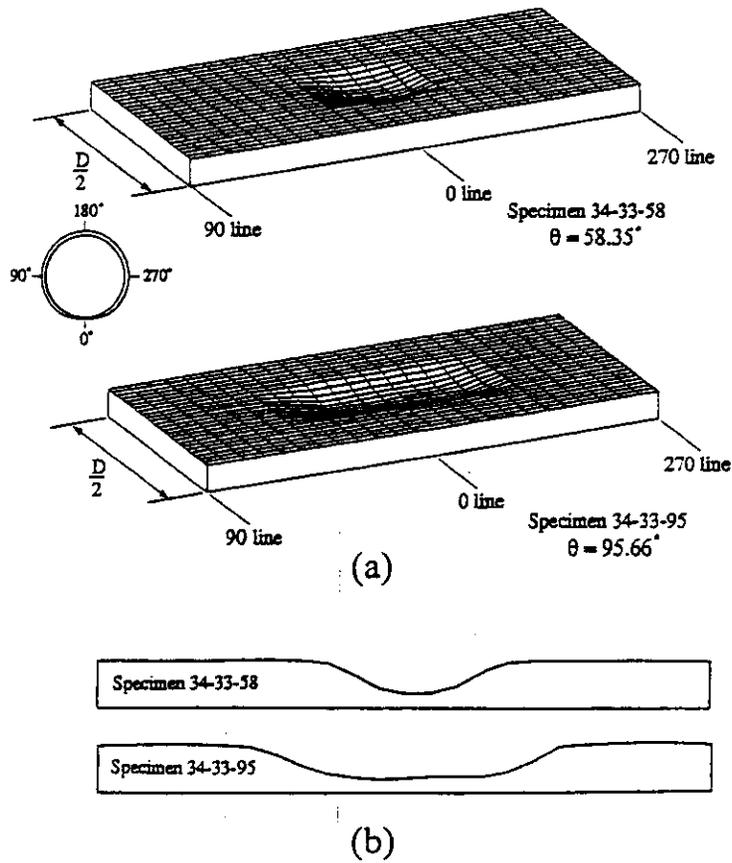
Fig. 5 Views of (a) Measured Wall Thickness Surface Plots and (b) Cross-Sectional Corrosion Profile for Selected Specimens

1994) showed that they had little effect, and in some cases actually increased the residual strength of patch corroded tubular members. The maximum difference in member capacity when accounting for residual stresses was found to be 2%.

Corrosion damage to the specimens was simulated by reducing the wall thickness by mechanically removing material with the use of a hand-held electric powered grinder. This simulation method was determined to be adequate, since corrosion is known not to cause any material property changes to tubulars having a yield strength less than 690 MPa. As noted previously, the contour of each specimen with corrosion had an idealized profile, consisting of zero slope at the most reduced area and at the edges of the corrosion patch (i.e., at the center and the edges of the ellipse of corrosion.). This contour was selected on the basis of idealized contours from measurements of actual corroded specimens (Ostapenko et al. 1993). During the grinding process, measurements were performed to ensure that the correct reduced wall thickness was obtained. These measurements of the corroded area were performed using a template of the corrosion profile in conjunction with ultrasonic methods. Ultrasonic thickness measurements for Specimens 34-33-58 and 34-33-95 are shown in Fig. 5 as an unfolded surface over a longitudinal length of $0.5D$. Thickness reduction values t_r for each specimen are given in Table 1, where they have been normalized by the original measured wall thickness t. The diameter, D, and wall thickness, t, of each specimen were also measured, with averaged values reported in Table 1. As noted above, the height h of each corrosion patch was equal to $0.5D$ (110 mm).

Each specimen was tested in a 2670 kN Satec overhead testing machine, as shown schematically Fig. 6. The instrumentation plan is also shown in Fig. 6, and consisted of a load cell to measure the applied axial load; transducers to monitor specimen axial shortening and radial movement of the corrosion patch due to local buckling; and strain gages to measure longitudinal strain in the steel tube. Each specimen was white washed before being tested in order to observe the development of yield line patterns.

The testing of each specimen commenced with load applied under displacement control at a rate of 0.25 mm/minute. The loading was stopped and the head displacement held constant at significant events, such as the onset of local buckling and maximum load, in order to obtain static load measurements. The test was terminated when either the specimen capacity had degraded to 80% below the peak axial load, or the specimen's axial shortening reached approximately 13 mm in the post-ultimate load range.

Typical response of a corroded specimen began with linear elastic behavior, and uniform longitudinal strain throughout the specimen. As the axial shortening was increased, the axial load also increased and the longitudinal strains in the corroded cross section became non-uniform. Conversely, the strains in the cross-section at a longitudinal distance of $0.5D$ away from the corroded cross section remained uniform. Yielding was observed to occur first in the corrosion patch with a subsequent pronounced local buckle forming at the center of the corroded patch. The ultimate load of the specimen was attained 3% to 5% above the load at which the local buckle first formed. For all specimens, except Specimen 34-33-58, the local buckle mode was an outward movement and resembled an "elephant-foot" mode, initiating at the center of the corroded area and propagating around the circumference. The local buckling in Specimen 34-33-
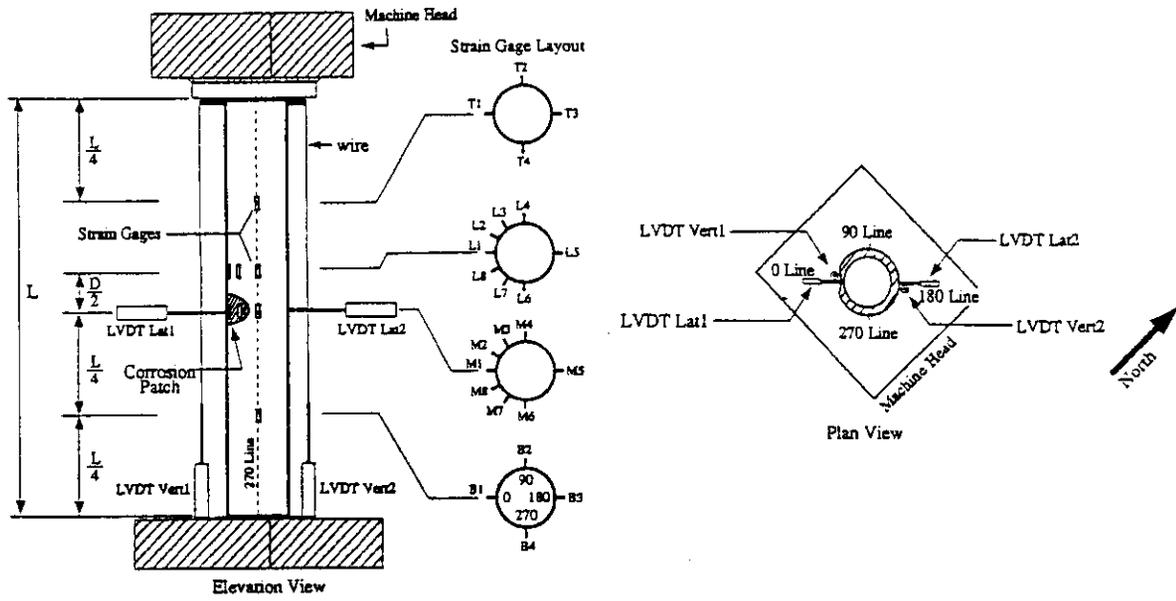
Fig. 6 Experimental Test Setup
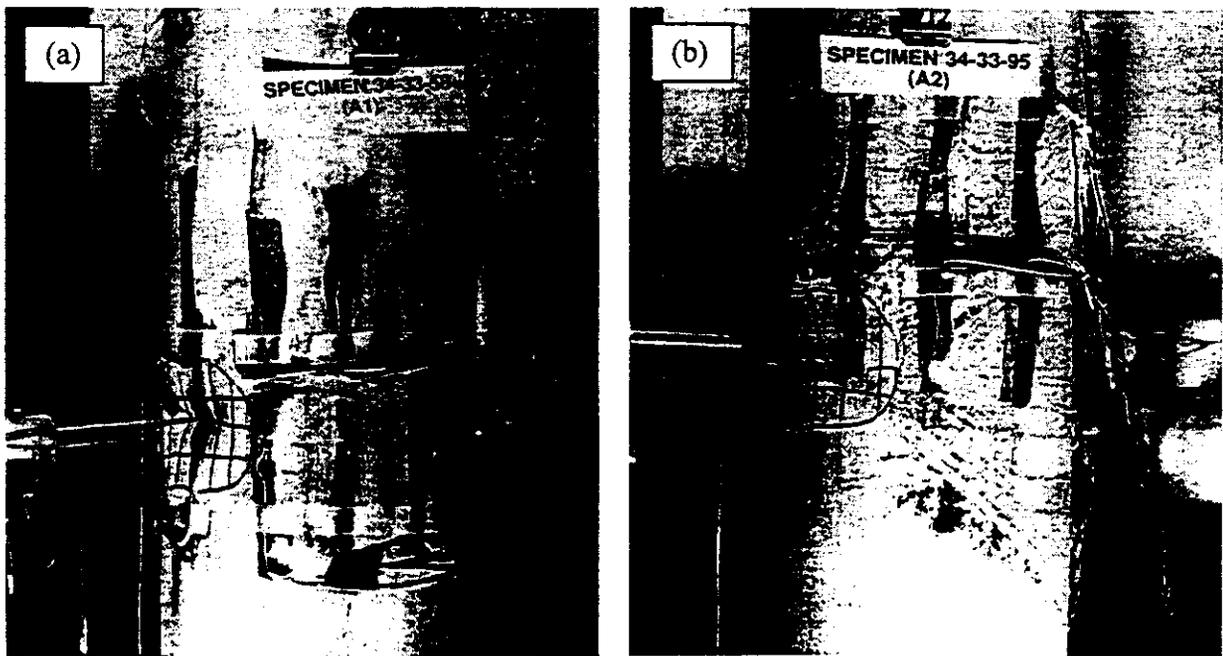
Fig. 7 Photographs of (a) Inward, and (b) Outward Local Buckling Mode in Corrosion Patch of Selected Specimens

58 caused an inward movement of the wall of the tube. The inward or outward mode of buckling was dependent on the aspect ratio (c/h) of the patch of corrosion. The corrosion patch for Specimen 34-33-58 had an aspect ratio close to 1.0, resulting in the inward local buckle becoming the critical mode. All other specimens had a corrosion patch with an aspect ratio of c/h ranging from 1.67 to 5.47, resulting in the outward local buckling mode. Both modes of local buckling are shown in Fig. 7.

As the axial deformation was continued, the buckling became more pronounced as it propagated around the circumference of the cross section. In addition, yielding became more extensive in the corroded cross section and also propagated around the circumference. The consequence of the yielding and local buckling was a loss of capacity, as shown in the axial load-deformation response of Specimen 46-33-95 given in Fig. 8.

A summary of the experimental axial load capacity $P_{u,exp}$ of each specimen is given in Table 2, where they have been normalized by the full axial yield capacity P_y. The experimental capacity of the non-corroded specimens (34-100-0, 46-100-0, 64-100-0) were all equal to 1.0 P_y. The axial load-deformation response of Specimen 46-100-0 is compared with that of Specimen 46-33-95 in Fig. 8, where it is evident that local buckling caused a significant loss of capacity in the corroded specimen. A comparison of the ratio of $P_{u,exp}/P_y$ of the corroded and corresponding non-corroded specimens in column 3 of Table 2 indicates that the loss of strength in corroded specimens with D/t=34 ranged from 8% to 32%, where a greater loss occurred for specimens with deeper corrosion (i.e., smaller t_r/t values) and wider corrosion patches (i.e., larger θ values). An examination of corroded specimens having D/t=46 and θ=95 degrees shows a reduction in capacity of 8% to over 21% compared to their corresponding non-corroded capacity. Specimen 46-33-95 is shown to have suffered a 19% reduction in strength due to corrosion. A comparison of this specimen with Specimen 34-33-95, where the latter has a lower D/t ratio but with the same extent of corrosion that resulted in a 17.5% capacity reduction, indicates that corroded specimens with larger D/t ratios have a larger capacity reduction due to the corrosion patch. The influence of the above parameters on the capacity of a corroded member will be discussed more later under the results of the analytical parametric study.

The experimental program to study the repair of patch corroded members consisted of the testing of two repaired specimens. The two repaired specimens were inflicted with the same corrosion as Specimen 46-00-95 so that a direct comparison of repaired and non-repaired specimen capacities could be made. With respect to each other, the two repaired specimens were identical except for the grout used to fill the annulus between the sleeve and the damaged tubular. One of the repaired specimens used a cement-based grout (Specimen 46-00-95-C), while the other used an epoxy-based grout (Specimen 46-00-95-E). The two repaired specimens and non-repaired Specimen 46-00-95 are shown in Fig. 9. Because the purpose of testing was to investigate a concept rather than a specific repair, the sleeve was not designed as it would be in practice, for the sleeve was not split into two halves nor were there any clamping brackets. The steel sleeve used for the repair had an inside diameter of 257 mm, a wall thickness of 9.5 mm, and a length of 267 mm. These sleeve and tubular dimensions produced an annulus between the tubular and the sleeve of 19 mm. To prepare the wall surface of the tubular for the repair sleeve,
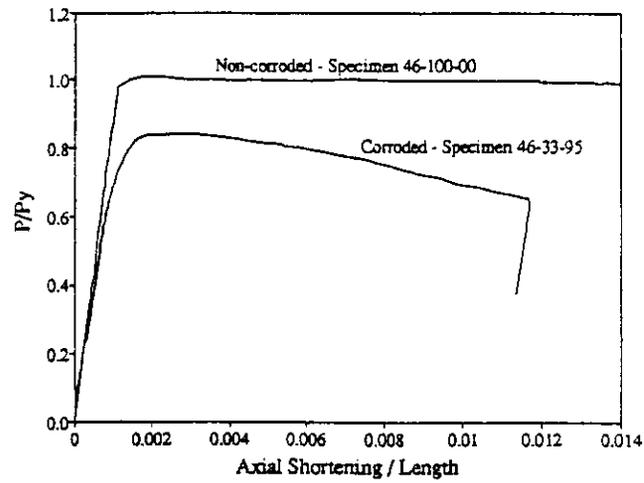
Fig. 8 Axial Load-Shortening Response of Selected
Corroded and Non-corroded Specimens
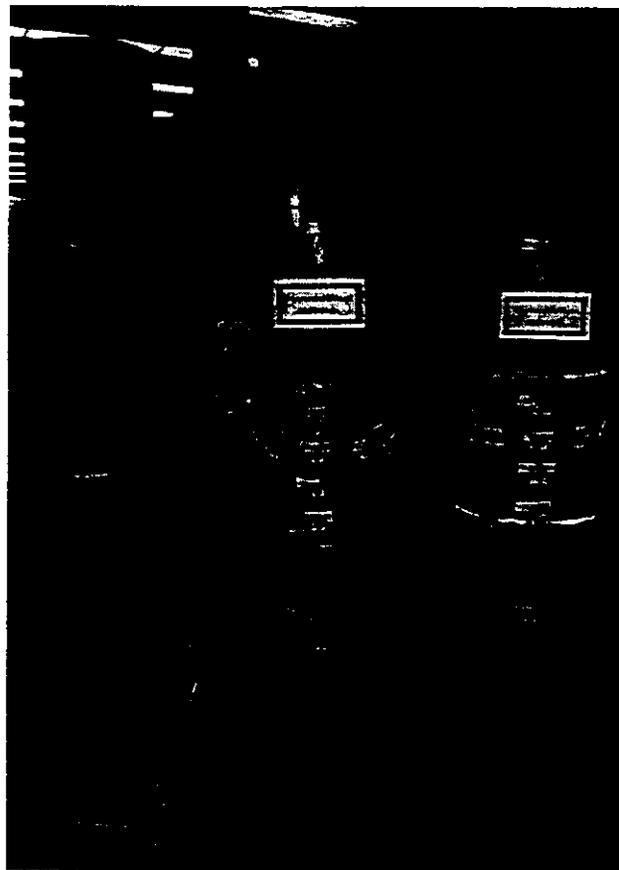
Fig. 9 Corrosion-Damaged Specimen 46-00-95, and
Repaired Specimens 46-00-95-C and 46-00-95-E

as well as provide a consistent, uniform surface roughness, the grout contact surfaces of the tubular and the sleeve were sandblasted to a consistent roughness of approximately 3 mils. Bond tests were conducted on push-out specimens for both types of grout. The bond stress-axial displacement relationship of the specimens is given in Fig. 10. The epoxy-based grout was found to have a bond strength that was 7.6 times greater than that of the cement-based grout. Material tests were also conducted to evaluate the compressive strength of the two types of grout. The compressive stress-strain relationships are shown in Fig. 11. The compressive strength of the epoxy-based grout was 1.8 time greater than that of the cement-based grout.

Table 2 Corroded Specimen Axial Load Capacity and Comparison with Analytical Results.

Specimen	P_y [kN]	$\dfrac{P_{u,exp}}{P_y}$	$\dfrac{P_{u,FEM}}{P_{u,exp}}$	$\dfrac{P_{u,sim}}{P_{u,exp}}$	$\dfrac{P_{u,reg}}{P_{u,exp}}$
34-100-0	1065	1.0	1.0	0.997	1.017
34-33-58	1071	0.916	0.969	0.978	0.968
34-33-95	1072	0.825	0.974	0.991	0.994
34-50-311	1054	0.684	0.966	0.849	0.894
46-100-0	859	1.0	1.0	0.997	1.005
46-00-95	858	0.783	0.922	0.928	0.899
46-33-95	858	0.809	0.973	1.01	0.999
46-67-95	861	0.924	0.988	0.984	0.992
64-100-0	614	1.0	1.0	0.997	0.982
64-60-95	614	0.856	1.0	1.04	1.02
46-00-95C*	858	1.0	-	-	-
46-00-95E*	858	1.0	-	-	-

*Repaired specimen

The test setup and instrumentation for the testing of the repaired specimens was similar to that for the non-repaired specimens, as shown previously in Fig. 6. However, additional strain gages were used in the repaired specimens. These included eight longitudinal strain gages around the circumference of the outside surface of the repair sleeve at mid-height, and eight longitudinal strain gages along the length of the sleeve on the 0 and 180 degree sides with respect to the circumference.

The non-repaired specimen (Specimen 46-00-95) had a static residual strength of $0.783P_y$, representing a capacity reduction of 21.7% compared to an undamaged tubular. The normalized axial load-shortening response of this specimen is plotted in Fig. 12, where it is compared to that of the repaired, as well as the non-corroded (46-100-00) tests. It is apparent from the normalized load-deformation plots in Fig. 12 that both repaired specimens, 46-00-95-C (Cement-based grout) and 46-00-95-E (Epoxy-based grout), were successful in reinstating the capacity to that of the undamaged member. For both of the repaired specimens the sleeve was stiff enough to provide proper hoop restraint to confine the cross section from buckling outward. Both repaired specimens failed by gross yielding of their cross section outside the sleeve repair.

(a)

Applied Load

Inner Steel Tubular

Grout

Outer Steel Sleeve

(b)

Slip

Fracture

Epoxy-Based Grout
Bond Strength Specimen

Residual Friction
Strength

Cement-Based Grout
Bond Strength Specimen

Bond Stress (psi)

Axial Displacement (in.)
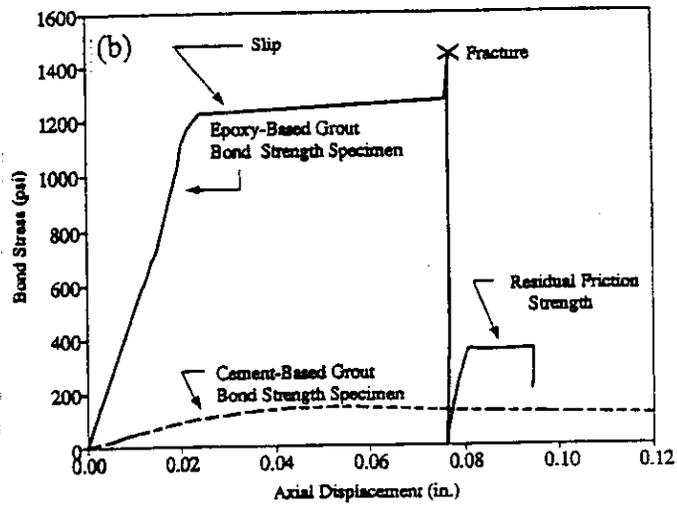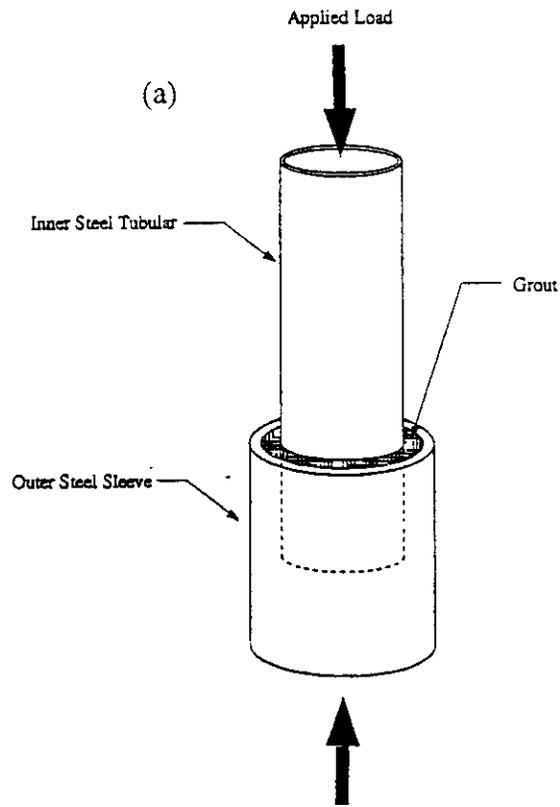
Fig. 10 (a) Bond Strength Push-Out Specimens, and
(b) Bond Stress - Axial displacement Relationships
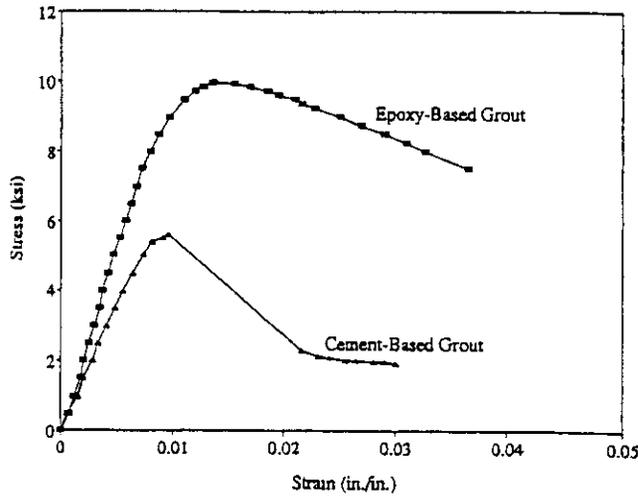
Fig. 11 Compressive Stress - Strain Curves for Epoxy-Based Grout & Cement-Based Grout
Cube Tests [Note: 1 ksi = 6.895 MPa]
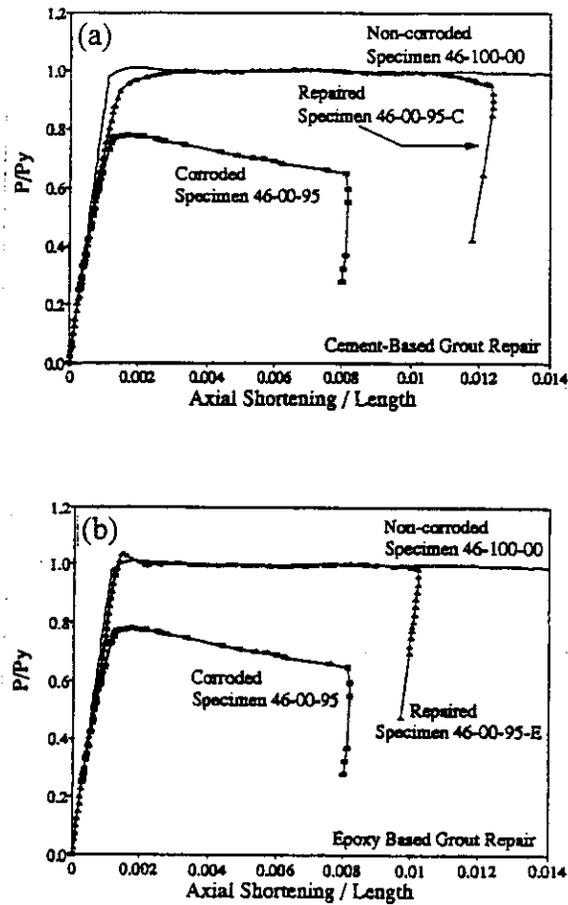
Fig. 12 Comparison of Axial Load-Shortening Response for Non-damaged and Corroded
Specimens with (a) Repaired Specimen 46-00-95-C, and (b) Repaired Specimen 46-00-95-E

While the ultimate load was not affected, there is a definite influence of grout bond strength on the behavior of the repair. The lower strength cement-based grout resulted in a more non-uniform longitudinal strain distribution (see Fig. 13(a)), yielding, an eventual inward local buckling of the corroded cross section, and an overall excessive lateral deflection of the specimen. These undesirable effects were caused by the lower bond (1.1 MPa) strength of the cement-based grout that could not preserve full compatibility between the tubular and the sleeve. These effects also account for the "softening" and nonlinearity of the load-deformation plot just prior to the ultimate load (see Fig. 12(a)). The damaged cross section still possessed an internal eccentricity and reduced gross section, leading to a reduced resistance to local buckling; however, the effects of these problems was minimized by the confinement of the sleeve. In contrast, the epoxy-based grout had a bond capacity (8.38 MPa) high enough to preserve the compatibility between the tubular and the sleeve, which prevented yielding and an inward local buckling of the corroded cross section. The normalized load-deformation plot in Fig. 12(b) is linear up to the ultimate load. It was found that the strain distribution was more uniform throughout the epoxy-based repair (see Fig. 13(b)) and that lateral deflections were reduced by over 80% compared to the cement-based grout repair.

Other positive aspects about the use of epoxy-based grout include the curing time and the inertness of the epoxy. The epoxy-based grout reached 80 to 90% of full strength in twenty-four hours (epoxy-based grout cubes exceeded 55.2 MPa in 24 hours), and reached full strength in seven days. In contrast, cement-based grout attains only minimal strength after twenty-four hours and needs 21 to 28 days to reach full strength. Furthermore, the epoxy-based grout is not influenced by contact with water, and can be used to displace water without detrimental effects. In contrast, the strength of the cement-based grout is highly dependent on the water-to-cement ratio. Therefore, the quality of the cement-based grout can be more affected by forcing it to displace water during a repair.

Analytical Program

The commercial finite element program ABAQUS (1993) was used to perform a finite element analysis of each of the non-repaired corrosion specimens. Material properties from the tensile tests and nominal dimensions of each specimen were used in the finite element models. Each model utilized an eight-node shell element in conjunction with measured material properties and dimensions to model the corroded, non-repaired specimen. The finite element analysis was based on an updated Lagrangian formulation to capture the effects of large displacements, and Green's strain and second Piola-Kirchoff stress to model the moderate strain levels and the corresponding stress conjugate. The von Mises yield criterion with isotropic strain hardening was used. The non-linear force-deformation response was obtained using the modified RIKS (1979) solution scheme.

Taking advantage of symmetry about mid-height and the cross section, and by using the appropriate boundary conditions, only one quarter of each specimen needed to be modeled (as shown in Fig. 14). The finite element mesh was refined in the area where corrosion existed (e.g. near mid-height of the specimens). A typical mesh had 350 shell elements, and 7000 degrees of
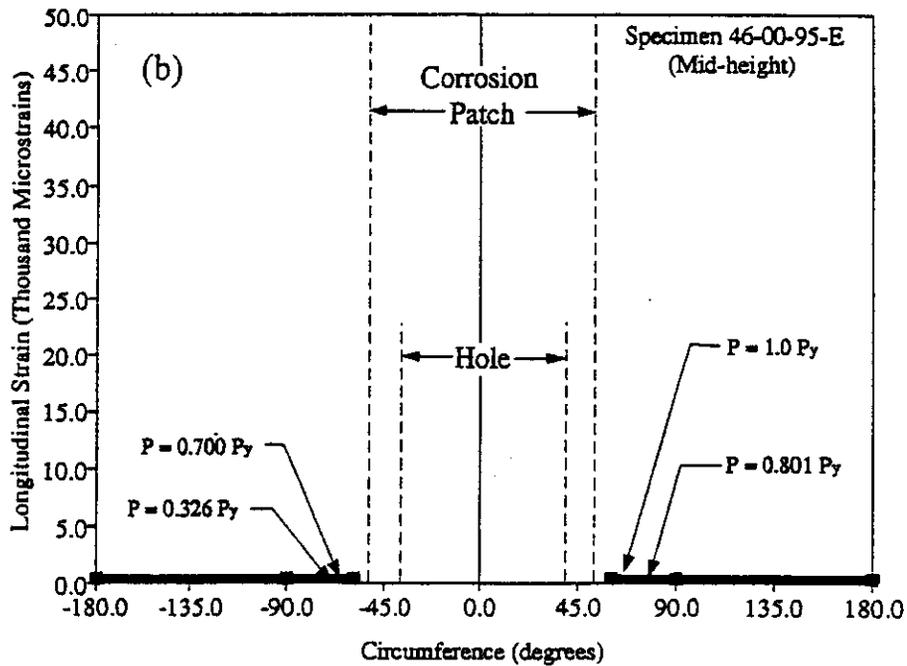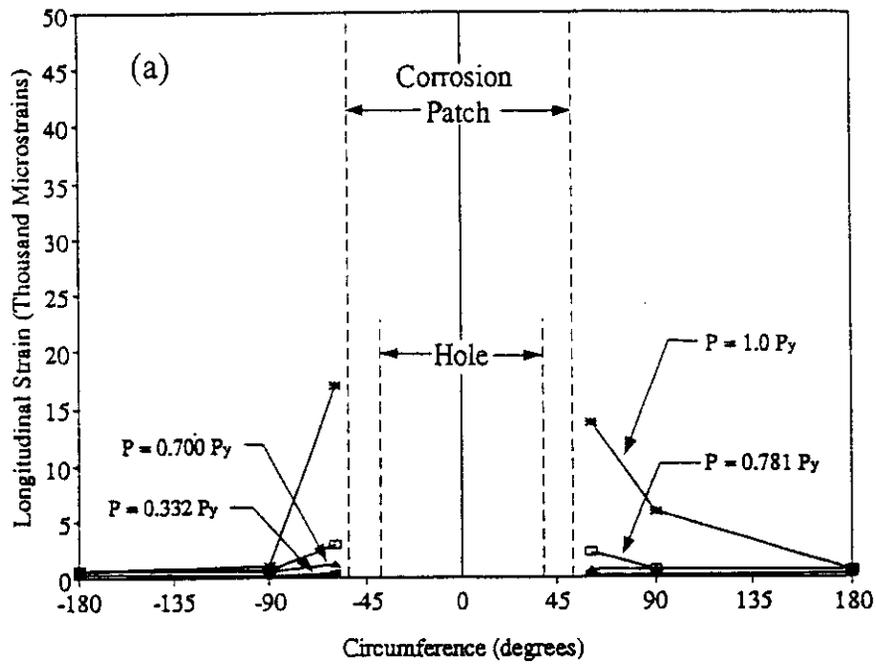
Fig. 13 Measured Longitudinal Strain Around Circumference of Cross - Section at Corrosion Patch for (a) Cement-Based Grouted Sleeve Repaired Specimen (Specimen 46-00-95-C), and (b) Epoxy-Based Grouted Sleeve Repaired Specimen (Specimen 46-00-95-E)
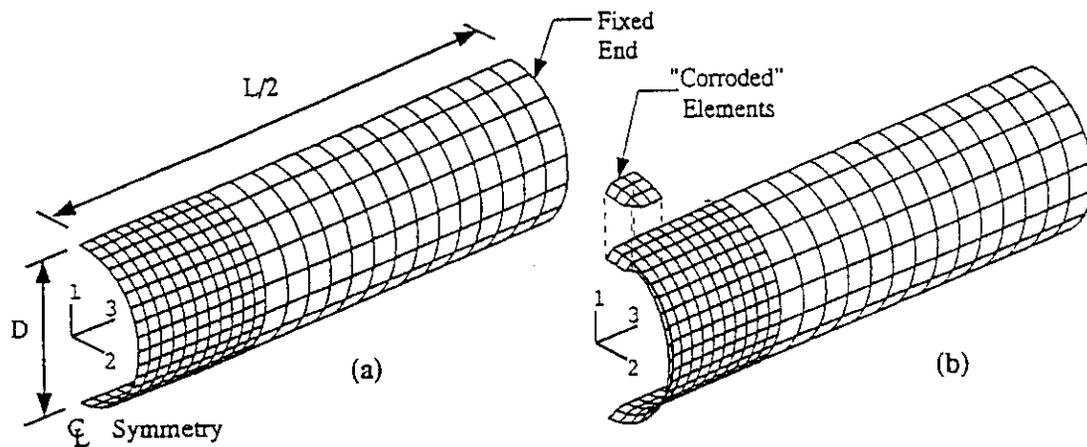
Fig.14 Finite Element Model of Corroded Specimen:
(a) Undeformed Model; and (b) Model with Local Buckling
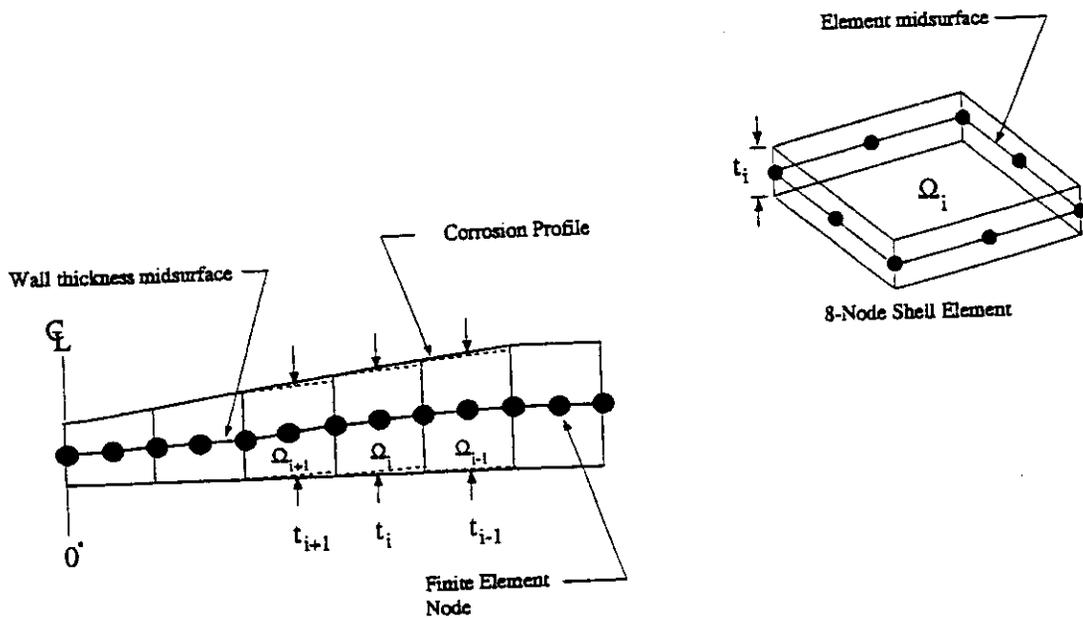
Fig 15. Placement of Nodes and Plate Element Wall Thickness for Modeling Corrosion Profile

freedom. The reduction of the wall thickness due to the corrosion was modeled, as shown in Fig. 15, by assigning each element Ω_i in the corroded area with an associated reduced thickness t_i and an associated mid-surface offset. Assigning coordinates to the element nodes corresponding to the appropriate offset created the mid-surface offset. Modeling the corrosion in this manner attempted to align the inside face of each element while staggering the outside face, simulating a thickness reduction occurring from the outside wall surface.

Several initial analyses were conducted to assess the sensitivity of the tubular member's capacity to the element mesh, particularly in the corrosion patch area. It was found that good agreement with experimental results was obtained when considering the thickness reduction to occur over a rectangular area of height h in the specimen's longitudinal direction which was equal to or greater than a critical value h_{crit} of approximately $0.5D$. The distance h_{crit} is associated with the minimum corroded distance for which the local buckle wave can form in the longitudinal direction of the specimen. This greatly simplified the analysis, for only the elements within the rectangular area of width $c=0.5D\theta$ and height h_{crit} needed to have a reduced thickness. As noted previously, the experimental study concentrated on corrosion patches with height h greater than h_{crit}, and therefore, the height of the corrosion patch was not considered as a parameter. For patch corroded tubular members with h less than h_{crit}, the assumption of h equal to h_{crit} would produce a conservative estimate of the residual strength.

A comparison of the predicted specimen capacity $P_{u,FEM}$ by the finite element analyses with the experimental result $P_{u,exp}$ for the non-repaired specimens is presented in column 4 of Table 2. The agreement is shown to be good, with the ratio of $P_{u,FEM}/P_{u,exp}$ ranging from 0.922 to 1.04, with a mean of 0.980 and a coefficient of variation (COV) of 0.024. The results for the finite element analysis and experimental study are also plotted in Fig. 16(a) where good agreement between the two is also evident.

A simplified elastic analysis for predicting the capacity of each non-repaired specimen was also performed. The centroid shift, e, the section modulus, S_d, and the area, A_d, of the corrosion-damaged cross section was calculated by discretizing it into 100 segments and summing the first and second moments for each segment about the geometric center of the cross section. The stresses from direct axial loads, flexure due to the centroidal shift, and fixed end moments, M_{FEM}, were then superimposed and equated to the yield stress of the specimen as follows:

$$\frac{P_u}{A_d} + \frac{P_u\,e}{S_d} - \frac{M_{FEM}}{S_d} = \sigma_y \tag{1}$$

The load, P_u, to cause the stress at the center of the corrosion patch to reach yield was then determined. This load was used as the estimate, $P_{u,sim}$, of the capacity of the specimen. The fixed end moments, M_{FEM}, were determined from analysis, and found to cause no more than a 3% increase in the predicted load, $P_{u,sim}$. The yield stress σ_y was used in Eqn. (1) in lieu of a theoretical local buckling stress σ_{cr} because all the specimens were observed to develop yielding in the center of the corrosion patch prior to when local buckling in the patch had occurred. This simplified elastic analysis produced reasonable results, which are listed in column 5 of Table 2

and shown in a correlation scatter plot with the experimental results in Fig. 16(b). The agreement between the predicted capacities and the experimental results is good, with values of the ratio $P_{u,sim}/P_{u,exp}$ ranging from 0.849 to 1.04 (see Table 2) with a mean of 0.977 and COV of 0.051.

<u>Parametric Study</u>

Several parametric analytical studies on non-repaired tubulars were performed in order to assess the effects of the geometrical parameters on residual strength, which describe the corrosion patch and tube. The parameters included t_r/t, θ, and D/t. Also included in these studies was the affect of the profile within the corrosion patch. Three profiles were studied, which had been referred to earlier (see Fig. 3), namely: (a) "step"; (b) "experimental"; and, (c) "cosine". The "cosine" and "step" profiles represent the upper and lower bound, respectively, associated with the member's local buckling strength for a given set of values for the parameters θ and t_r/t. The purpose of investigating profile effects was to assess the difference between these two bounds since it is likely that the thickness profile cannot be measured accurately in the field. Consequently, it may be desirable to assume the "step" profile if it is not overly conservative.

Shown in Fig. 17 are selected results associated with the "experimental" profile and where $h=0.5D$. Each set of results presented in Fig. 17(a), (b), and (c) represents a series of analysis where two of the three parameters t_r/t, θ, and D/t were held constant, and the third varied. The ensuing relationships between the normalized member capacity P_u/P_y and the independent parameter that was varied, either t_r/t, θ, or D/t, are each known as coordinate functions. Fig. 17 indicates that each of these coordinate functions is linear. Furthermore, the member local buckling capacity P_u/P_y is shown to be significantly sensitive to the parameter θ (see Fig. 17(a)) and t_r/t (see Fig. 17(b)), whereas it is not as sensitive to the member's D/t ratio (see Fig. 17(c)).

The linear coordinate functions were combined using a multi-variable regression analysis to obtain a closed form expression for P_u/P_y as a function of the parameters t_r/t, θ, and D/t, where:

$$P_u/P_y = 1.0 - 0.001 \left(\frac{D}{t}\right) + 0.052 \left(\frac{t_r}{t}\right) - 0.0026 \left(\theta\right) + 0.0028 \left(\frac{t_r}{t}\right)\left(\theta\right) \tag{2a}$$

where

$$34 \leq \frac{D}{t} \leq 100; \quad 0 \leq \frac{t_r}{t} \leq 1.0; \quad 58^{\circ} \leq \theta \leq 311^{\circ} \tag{2b}$$

A comparison of the experimental specimen capacity $P_{u,exp}$ and the predicted value $P_{u,reg}$ by Eqn. (2a) has the ratio of $P_{u,reg}/P_{u,exp}$ ranging from 0.894 to 1.02, see Table 2, with a mean of 0.977 and COV of 0.044. These results imply that good agreement exists between the predicted and experimental capacities. A comparison between the experimental and regression analysis capacity predictions is shown in Fig. 16(a). The comparison between the finite element analysis results for member capacity $P_{u,FEM}$ and $P_{u,reg}$, in which the former was used to create the database for the regression analysis, is given in Fig. 16(c). The agreement between $P_{u,FEM}$ and $P_{u,reg}$ is
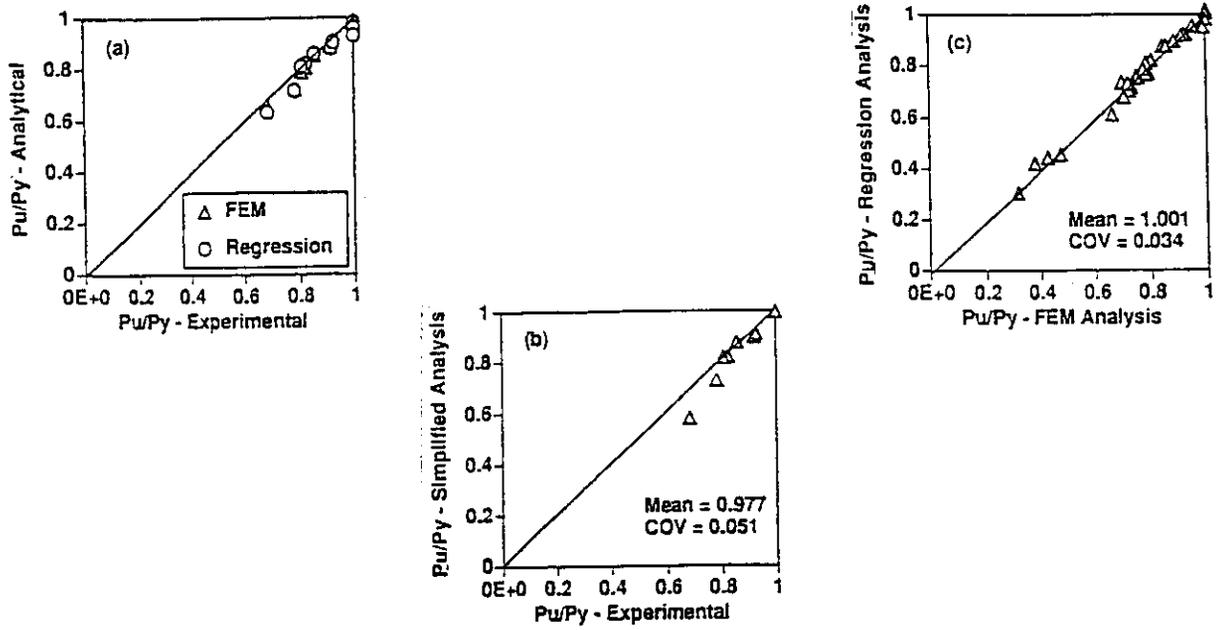
Fig. 16 Comparison of Experimental Capacity with (a) FEM and Regression Analysis and (b) Simplified Analysis, Comparison of (c) FEM Results with Regression Analysis
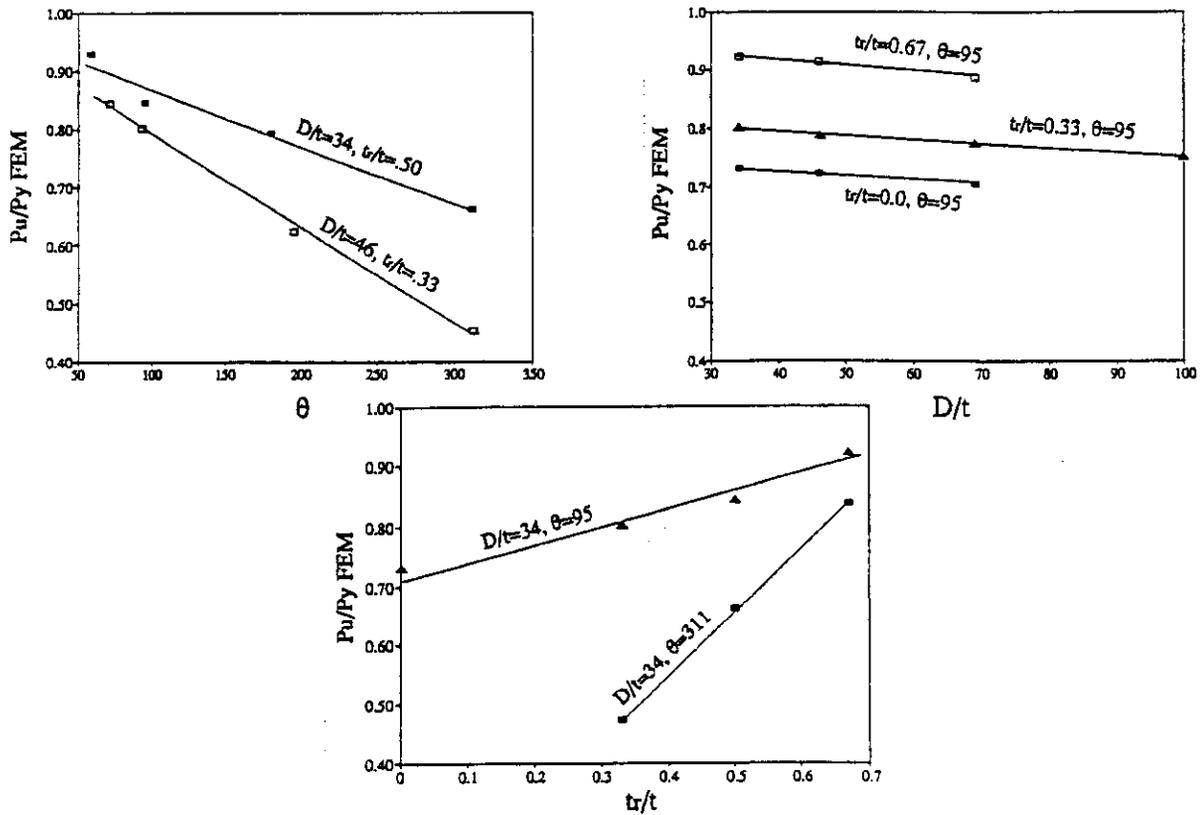
Fig. 17 Variation of Predicted Capacity (FEM) as a Function of Corrosion Parameters, In Conjunction with Experimental Corrosion Profile
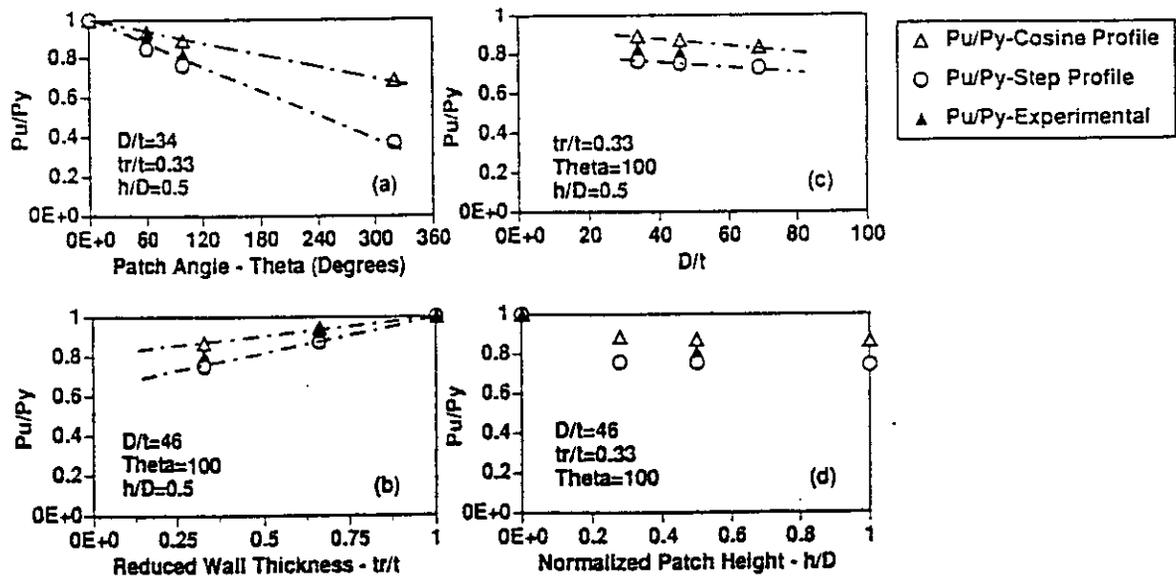
Fig. 18 Variation of Predicted Capacity (FEM) as a Function of Corrosion Parameters and
Comparison with Experimental Results

generally good, where the ratio $P_{u,reg}/P_{u,FEM}$ varies from 0.925 to 1.115 with a mean of 1.001 and COV of 0.034.

The affect of the thickness profile within the corrosion patch on member local buckling strength P_u/P_y is shown in Fig. 18, where the coordinate functions are plotted for member strength with θ, t_r/t, and D/t as the independent variables, respectively, for the "step" and "cosine" profiles. Fig. 18(d) shows the affect of the normalized patch height h/D on P_u/P_y, where the experimental data has been included, and is identified as "P_u/P_y - *experimental*". The results in Fig. 18(d) show that for both the "step" and "cosine" profiles that the decrease in strength P_u/P_y is constant for a patch height h greater than or equal to 0.5D. The maximum discrepancy in P_u/P_y is 14% between the results based on the upper and lower bounds computed using the "step" and "cosine" profile. The experimental data is within 7% of these two bounds. The remaining coordinate functions (Figs. 18(a), (b), and (c)) are shown to be linear for both profiles, with the difference in value for P_u/P_y between the two becoming larger as the corrosion patch width (θ) and depth (t_r/t) increase, respectively (see Fig. 18(a) and (b)).

The discrepancy in the prediction for P_u/P_y using the "cosine" and "step" profiles is 10% and 14% for $\theta=60^0$ and 100^0, respectively, and increases to 45% for $\theta=320^0$ (see Fig. 18(a)). The latter case, in which $\theta=320^0$ and $t_r/t=0.33$, is a significant corrosion case. The difference in value for P_u/P_y is much less when varying the value for t_r/t, where the predicted strength P_u/P_y based on the "step" and "cosine" profiles is within 7% and 12% of each other when t_r/t is equal to 0.66 and 0.33, respectively (see Fig. 18(b)). The difference in the predicted value for P_u/P_y using the two "step" and "cosine" profiles remains fairly constant as the D/t ratio increases, being equal to about 13% (see Fig. 18(c)). In all cases, the experimental data is bounded by the 'step" and "cosine" profiles, and is within 7% of these bounds.

Although there is some difference in the predicted strengths using the "cosine" and "step" profiles, actual corrosion patch profiles will fall in between these profiles and the predicted strengths from them will bound the actual capacity. An assessment of the results presented in Fig. 18 indicates that the difference in the results for P_u/P_y based on the two bounds is at most 14% when θ is less than 120^0, where the patch width c is one-third the member circumference (i.e., $c=0.33D$), and anticipated to be 26% when $\theta=180^0$ (corresponding to $c=0.5D$). Considering other uncertainties associated with the analysis of an offshore structure, including wave load estimation as well as structural modeling of members and the foundation, and the difficulty in accurately measuring a corrosion profile, it may be practical to conservatively use the "step" profile in assessing the local buckling strength.

SUMMARY AND CONCLUSIONS

The results of an experimental and analytical study on the residual strength of short steel tubulars with idealized patch corrosion subjected to concentric axial load indicated that a significant reduction in capacity occurs due to the initiation of local buckling in the corrosion patch. This local buckling is attributed to the effect of a reduced wall thickness, combined with an amplification of stress at the corroded area due to a shift in the centroid of the cross section.

Nonlinear finite element analysis showed the corroded specimen capacity to have linear coordinate functions with respect to the corrosion parameters t_r/t, θ, and D/t. The shape of the wall thickness profile within the corrosion patch has an affect on the local buckling strength, but was found not to be as significant as the need to use accurate values for the parameters θ and t_r/t. The local buckling strength in the corrosion patch is independent of the height of the patch h, provided that the corrosion height is equal to or greater than $0.5D$. A multi-variable regression analysis resulted in a semi-empirical expression for predicting the axial load capacity of short, patch-corroded steel tubulars. The use of a simplified elastic analysis also provided reasonable approximations of the residual strength. The exterior grouted sleeve repair was found to successfully reinstate the full capacity of a corrosion-damaged tubular member. Confinement of the corroded cross-section is the primary mechanism for a successful repair, and low bond strength grouts may be used for sleeve type repairs. However, epoxy-based grouts are more capable of preventing yielding and buckling of the damaged cross section because of their higher bond strength. High bond strength grout should be used, particularly when the possibility of inward buckling of the corrosion patch exists.

ACKNOWLEDGMENTS

REFERENCES

1. *ABAQUS User's Manual (Version 5.3)* (1993), Copyright Hibbitt, Karlsson and Sorensen, Inc., 100 Medway Street, Providence, Rhode Island, 02906.

2. Cole, M.W., Marucci, T.F. and Taft, D.G., (1987), "MODU Marine Safety: Structural Inspection and Readiness Surveys," *Journal of Petroleum Technology*, Society of Petroleum Engineers, Vol 11.

3. Dunn, F. P. (1983), "Offshore Platform Inspection", Proceedings, *International Symposium on the Role of Design, Inspection and Redundancy in Marine Structural Reliability*, Marine Board, National Research Council, National Academic Press.

4. Galambos, T. V. (1988), *Guide to Stability Design Criteria for Metal Structures*, Fourth Edition, Wiley-Interscience Publication, New York, New York.

5. Hebor, M., and Ricles, J. (1994), "Residual Strength and Repair of Corroded Marine Steel Tubulars," *ATLSS Report No. 94-10*, ATLSS Eng. Research Center, Lehigh University, Bethlehem, Pennsylvania.

6. Ostapenko, A., Wood, B., Chowdhury, A. and Hebor, M. (1993), "Residual Strength of Damaged and Deteriorated Tubular Members in Offshore Structures", *ATLSS Report No. 93-03*, Lehigh University, Bethlehem, Pennsylvania.

7. Paterson, D., (1999), "Residual Strength and Repair of Corroded Marine Steel Tubulars Subjected to Cyclic Loading," *M.S. Thesis,* Department of Civil and Environmental Engineering, Lehigh University, Bethlehem, Pennsylvania (in progress).

8. Riks, E. (1979) "An Incremental Approach to the Solution of Snapping & Buckling Problems," *International Journal for Solids and Structures,* Vol. 15.

9. "Test Methods for Tensile Coupon Testing" (1991), *ASTM Special Technical Publication E8-91*, ASTM, Philadelphia, Pennsylvania.

10. "Test Methods for Compressive Strength of Hydraulic Cement Mortars" (1992), *ASTM Special Technical Publication C109-02*, ASTM, Philadelphia, Pennsylvania.

Corrosion and Materials Challenges for Deep Water Oil and Gas Production

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FOR DEEP WATER OIL AND GAS PRODUCTION

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ABSTRACT

In recent years, there has been a substantial increase in oil and gas exploration and production in deep water regions. These expanded operations have involved many new challenges that have necessitated engineering changes, design adaptations and selection of alternative materials and systems. A major area that has been affected by the current boom in deep water operations is corrosion and materials technology. This paper presents a discussion of the changes in corrosion and materials technology required for deep water operations. These include the use of: (1) alternative alloys to resist corrosion in production environments, (2) higher strength materials for structures, tubulars and flowlines, (3) weight saving materials and composites, (4) flexible materials for flowlines and risers and (5) cathodic protection system design. This paper also highlights specific developments in each of the abovementioned areas.

INTRODUCTION

There has been major growth in offshore development of oil and gas reservoirs which, in recent years, has moved into progressively deeper waters (See Figure 1).[1] In many cases, drilling and production operations in deeper waters have resulted in new engineering challenges particularly from the standpoint of requirements for mitigating corrosion. As water depths have increased, so have costs associated with conventional means of corrosion protection. Examples are the use of corrosion inhibitors and conventional cathodic protection designs. The cost to implement corrosion inhibition in deep offshore areas in many cases has become economically prohibitive. This has resulted in the use of alternative materials with inherent resistance to corrosion in production environments containing H_2S and high levels of CO_2. Cathodic protection of structure in deep water has also required changes in design practices aimed mainly toward making the cathodic protection system more efficient and cost effective.

In addition to changes directly driven by cost factors, changes in corrosion mitigation strategies for deep water developments have also been based on reliability. Deep water wellhead system, pipelines and structures are expensive and typically require long term successful operations to achieve payout. Therefore, once corrosion protection methods have been implemented, they must provide long term reliability for up to 30 years or in some cases longer. Finally, repair costs have also increased dramatically with water depth to the point that sometimes a single failure can result in direct and associated costs in the range of $10 to 100 million.

In response to the changing offshore technical and economic environment, changes in materials selection and corrosion mitigation strategies have been developing. This paper identifies several areas where advances have been made and are continuing. It presents results of a survey of major oil companies which have led the charge into deep water oil and gas development. This paper focuses on the following topics identified to be essential for successful deep water development and operations:

1. High Strength Materials
2. Corrosion Resistant Materials
3. Weight Saving Materials
4. Engineered Materials Systems
5. Cathodic Protection

CORROSION RESISTANT MATERIALS

Effective mitigation of corrosion of downhole and surface components and systems exposed to oil production environments has been conventionally achieved with the use of corrosion inhibitors and, in some cases, internal coatings. In deep water operations, however, this conventional technology has serious limitations relative to the following areas:

1. *Logistics* - Costs of providing a continual supply of corrosion inhibitor to remote satellite platforms and subsea production system is high and increases greatly with water deep.
2. *Weight and space* - Effective inhibition in deep wells, often requires continuous injection. These facilities are an added burden to platforms which have serious space and weight limitations.
3. *Monitoring* - Corrosion inhibition programs need monitoring which is difficult in remote areas and is manpower intensive. Additionally, inhibitor procurement must also be monitored so that changes in formulation and inhibitor performance can be identified with time.
4. *Long Term Reliability* - Inhibitor programs rarely stop corrosion but merely reduce it to a rate that results in an *acceptable* service life. Usually this is between 5 and 10 years with workovers at planned intervals. With the increasing project life and desires to reduce or eliminate workovers as associated costs, longer term reliability is a major requirement.

As an alternative to the use of conventional technology involving steel and inhibitors, alloys have been developed which have resistance to the corrosive and embrittlement effects of H_2S and CO_2. Concerns have been on well environments that typically contain high partial pressures of CO_2 or CO_2 in combination with low to moderate H_2S partial pressures. In such cases, stainless steels can be cost effective, longer term alternatives to inhibitors. The use of corrosion resistant alloys (CRAs) allows for corrosion to be effectively reduced to less than 0.05 mmpy. However, this requires substantial knowledge of the performance limits of these materials and long term well production characteristics. This includes being able to evaluate changing well conditions over the entire life to identify worse case conditions of water production, flow conditions and workover and well stimulation requirements. Computer models are now available to assess and predict the corrosion rates of steel and the efficacy of inhibitor treatments (PREDICT®)[2] and the

performance of CRAs (SOCRATES®)[3] through specification of various operational parameters of the production environment.

Alloys of high current interest in offshore applications are indicated in Table 1 and are include:

1. **13Cr martensitic stainless steels** - This alloy is cost effective since they can be made with similar manufacturing methods used for conventional carbon and low steels. However, they are mainly utilized for resistance to CO_2 corrosion and have limitations in the amount of H_2S they can handle due to susceptibility to sulfide stress cracking (SSC).
2. **Modified 13Cr stainless steels** - These materials are based on 13Cr composition but depend on alloying additions of Ni and Mo to increase corrosion resistance at high temperatures and in applications involving higher H_2S partial pressures. More importantly, resistance to SSC is improved over 13Cr.
3. **Duplex stainless steels** - These materials come in 22 Cr and 25Cr varieties and derive their name from their duplex microstructure containing approximately a 50:50 blend of ferrite and austenite. They have higher Cr and Mo content along with N and sometimes W additions and require different processing methods. Consequently, they are correspondingly more expensive than 13Cr alloys. They have higher strength capabilities due to cold working and greater resistance to corrosion than these other materials. They offer advantages in many offshore applications.
4. **Austenitic stainless and nickel-base alloys** - These include a broad range of materials including higher alloy stainless steels and nickel base alloys. They are typically utilized in applications where very high H_2S partial pressures are being experienced. They have very high levels of Cr. Ni, Mo and sometimes N, W and/or Nb.
5. **Titanium alloys** - There are many very corrosion resistant Ti-alloys available which also provide high specific strength (i.e. low density and high strength). Ti-alloys include Grades 2 through 29 and are available in a range of strengths up to about 120 ksi. Current vintage alloys can have additions of Ruthenium (Rh) or Palladium (Pd) to enhance resistance to localized corrosion in seawater applications and in exposure to hostile production environments.

The main limitations in use of these newer or modified alloys is the lack of long term operating experience. However, limited service experience has been supplemented by accelerated laboratory tests conducted under closely simulated service conditions. This has helped to define longer-term corrosion performance and operational limits within which these materials can be utilized.

HIGH STRENGTH MATERIALS

One of the paramount needs in deep water applications is the requirement for higher strength materials in many areas of application including:

1. Downhole oil country tubular goods (OCTG)
2. Drill pipe
3. Risers

4. Linepipe
5. Constructional steels.

Weight savings in deep water applications is critical. One way to accomplish this is with higher strength materials that increase load carrying capabilities while decreasing wall thickness and section size. This approach has helped to extend drilling and production systems into deeper water.

For offshore platforms and structures, higher strength steels must be used. This requires developments in steel making technology which includes the use of thermo-mechanical controlled processed (TMCP) and microalloyed (MA) steels to achieve grain refinement, uniform through wall hardening and uniform microstructures resulting in higher strengths. Steel tendons for tension leg platforms can now be routinely made with yield strengths in excess of 770 MPa. Hydrogen embrittlement (Figure 2)[4] and accelerated fatigue crack growth rates (Figure 3)[5] have been a concern in these materials due to the production of hydrogen by either cathodic protection or resulting from seawater contaminated with H_2S from bacterial growth. Efforts have been made to control excessive cathodic protection (CP) currents through more efficient design of CP systems. Also, the use of metallurgical processing to control the microstructure has helped to enhance fracture toughness and resistance to cracking.

In deep water applications, higher strength (Y.S. - 500-900 MPa) plate steels must be utilized that have good weldability and maintain their strength and toughness following welding with minimum requirements for post weld heat treatment. One problem first experienced in the 1980's with steels for deep water platforms was obtaining acceptable strength and toughness following welding. Problems associated with excessive weld heat affected zone (HAZ) hardness, brittle course grain HAZ and softened base metal regions adjacent to the HAZ complicated performance. Current vintage TMCP steels have over come many of these problems with limits on MA content and ratios of various MA elements have been taken into account.

For downhole tubulars, C-110 grade sour service grades of steel OCTG are now available from several suppliers which provide higher strength (Y.S. - 760-860 MPa). As shown in Figure 4, these materials retaining resistance to sulfide strength cracking (SSC), a common problem common to high strength steels exposed to H_2S-containing production environments.[6] These materials typically require optimum metallurgical processing and quality control to produce a fine grained, quenched and tempered microstructure through alloying additions of Cr and Mo and MA additions of V, Ti, Nb and B combined with restricted maximum hardness.

Many corrosion resistant stainless steels and alloys have yield strengths that are only 50 to 70 percent of conventional steels. However, progress has been made in modified alloy compositions and processing that effectively increase the useable strength of these materials. One area where this has been over high interest is in OCTG and pipeline materials. For example, 13Cr stainless steels typically have yield strength limits in the range of 550 to 650 MPa. But now, modified 13Cr alloys with lower carbon content, 4 to 6 percent Ni, 1 to 2.5 percent Mo allow for tubulars with high corrosion resistance combined with yield strengths up to 760 MPa which are also

tolerant to moderate levels of H_2S (See Figure 5).[7] For pipeline applications, 22Cr and 25Cr duplex stainless steels can be attractive alternatives in some high CO_2 applications relative to steel that must be used with inhibitors. With H_2S limits similar to those of 13Cr materials, these materials can be used in the annealed and welded conditions up to about 620 MPa yield strength for piping and topside equipment. They can also be coldworked for use as OCTG to yield strength levels up to 950 MPa.

WEIGHT SAVING MATERIALS

As discussed previously , one way to push existing offshore systems and technology into deep water is to use higher strength materials. However, this is not always possible and alternative materials which provide lower weight must be utilized. In the search lighter system, engineers have taken some the developments of aerospace designers which have included both metallic and non-metallic materials high combine high strength and low weight. In terms of rise components Ti-alloys are very attractive as a result of a density that is about 60 percent of that of steels. Some alloys such as Ti-6Al-4V and Beta-C can also be processed by heat treatment to over 830 MPa yield strength levels further adding to their utility. These materials have been used in risers and swivel components that must have a combination of flexibility and high strength as well as resistance to corrosion (See Figure 6).[8]

However, one concerns with titanium alloys has historically been resistance to hydrogen embrittlement when used in systems under cathodic protection. Ti-alloys have limited solubility for atomic hydrogen and can be susceptible to hydride formation to varying degrees based on their composition and microstructure and the level of hydrogen charging. Embrittlement due to hydrides increases with increasing cathodic potentials beyond -700 mV SCE. Therefore in seawater applications, limiting CP potentials can increase resistance to hydride formation. Additionally, contrary to what is known about steels and SSC susceptibility, lower strength α-Ti alloys such as Grade 2 are the most susceptible to hydrogen embrittlement whereas alloys containing mixed $\alpha+\beta$ structures (Ti-6Al-4V) offer generally higher resistance with β-Ti alloys (Ti-Beta C) having even higher resistance. The resistance of equipment made from Ti-alloys to hydrogen embrittlement can also be improved by oxidation treatments that thicken the titanium oxide surface layer. This effectively provides a diffusion barrier on the metal surface that is very impervious to hydrogen diffusion at normal oilfield operating temperatures.

Another avenue being pursued in an effort to obtain lighter, high strength and more flexible structures is with the use of fiber composites. Examples of such uses include platform topside structures, vessels, tanks and piping. New grades of fiber reinforced plastic (FRP) pipe products been developed for seawater injection and downhole production service. Most of the materials are based on chemically resistant polymeric epoxy and polyester resins strengthened with glass, kevlar or carbon fibers which are light weight and yet provide high ultimate strength. Typical materials have up to 30 times the strength of steel and 15 times that of aluminum. Due to cost factors, mostly glass and organic fiber materials utilized in oilfield applications. However, carbon fibers are finding increased application especially in critical areas as manufacturing costs come down. The strength and elastic modulus of FRP products and equipment can often be optimized

for specific applications using sophisticated fiber lay-up techniques which place the fibers in the orientations of high tensile stress.

Fiber composites are very serviceable, however their differences from conventional materials must be realized. While being high strength, polymeric materials have more serious wear and temperature limitations than do metallic materials. Design temperature limits for polymers range up to about 120 C for most common materials. They are also often damaged unnecessarily during installation or use because they generally do not have the ductility, impact or abrasion resistance of steel. Chemical compatibility is also an important issue with polymeric materials particularly when longer term serviceability is critical. These materials can absorb moisture and other chemicals and also be affected by UV exposure. These effects can produce time dependent degradation of mechanical properties which can reduce serviceability limits as a function of time (See Figure 7).[9] Therefore, it is important to know how the performance of FRP materials vary with age and operate within these limits. A variety of test ASTM and NACE methods are available for evaluation of aging in these materials.

ENGINEERED MATERIALS SYSTEMS

One of the advances made within the past several years has been the use of engineered materials systems which bring together specific performance properties of various materials to perform specific functions not previously possible by conventional materials. These types of systems have made a significant impact on offshore operations particularly in the quest for deeper water production. Three types of engineered materials systems which have extended offshore depth capabilities are:

1. Umbilical lines
2. Flexible pipe
3. Risers

Examples of these systems are shown graphically in Figure 8.[10] They have utilized many of the elements of the materials and corrosion technologies given in this presentation combining materials with corrosion resistance, high strength, low weight and flexibility.

A particularly good example of how the abovementioned attributes have been integrated into a single product is illustrated in flexible pipe products such as that shown schematically in Figure 9. It is used for many offshore applications including flexible flowlines linking subsea production and wellhead systems to satellite platforms. Flexible pipe can be reeled for easy transport and field installation. It utilizes multiple ply construction to incorporating high strength steel armor and strength plies, polymeric materials and corrosion resistant alloys. A typical lay-up and cross-section of a section of flexible pipe is shown in Figure 10. The system shown involves eight metallic and non-metallic layers to provide resistance to corrosion, wear and collapse resistance in combination with high tensile strength, flexibility and a barrier to gases and fluids. This is no simple task particularly when the environment contains raw well fluids with high levels of corrosives such as H_2S, CO_2 and brine. Concerns for this system have been resistance of the strength steel plies to HIC and SSC. However, substantial development effort has been made to

qualify materials in standard H_2S-containing solutions (NACE TM0177 and TM0284) and various simulated service environments. This work has required the careful selection of steel composition, heat treatment and welding procedures to optimize cracking resistance when exposed to H_2S.

CATHODIC PROTECTION

One of the most basic corrosion prevention technologies making offshore operations possible has been cathodic protection. This technology utilizes application of a cathodic polarization originating from either sacrificial anodes or impressed current to the pipe or structure submerged in seawater. This cathodic current works counter to the normal electrochemical corrosion reaction and thereby reducing corrosion rates of the steel cathode to a tolerable level. Local shifts in the pH at the cathode to more alkaline levels also assists in limiting corrosion by inducing the formation of a calcareous scale. In shallow water, cathodic protection system designs are relatively simple, easy to maintain and come with substantial experience in many locations around the world. However, with the advent of deep water operations, there has developed a greater emphasis on design for long term service and reliability. Retrofitting anodes on depleted or poorly designed CP systems in deep water is usually an expensive endeavor. Likewise, with the weight constraints on new deep water platforms, costly over-design of sacrificial anode systems must also be prevented Therefore, greater initial effort is needed to understand the complexities associated with deep water systems.

For example, shallow water systems up to about 200 meter water depths can usually be handled with existing CP technology. Industry standards and years of experience are available which make design of CP systems straight forward. However, for deep water structures, the range of ambient conditions is subject to greater variation with water depth. The local conditions such as water temperature, oxygen content, pH and resistivity may be much different on the sea floor than at the surface. Therefore, the CP system usually has to be designed in zones specifically focusing the CP design for shallow, medium and deep portions separately.

One of the most dramatic effects is the difference in cathodic protection requirements in deep water versus at the surface. Generally, the low temperature (5-10 C) sea bottom conditions result in changes seawater resistivity which is a major factor in CP design. Additionally, the tendency to form protective calcareous deposits on the steel also varies with depth. In the colder seawater, there is a reduction in the rate of calcareous deposition and the composition changes as a result of increased solubility of $CaCO_3$ and decreased $Mg(OH)_2$ (See Figure 11).[12] These changes reduce calcareous deposition at low temperature which, in turn, can change polarization characteristics and increase CP current requirements.

The cathodic protection criteria provided in NACE RP-01-76 that are widely used in shallow waters still apply for deep water applications. The difference comes in the greater current requirements to achieve these criteria in deep water as a result of the decrease in protection obtained from calcareous deposition and changes in seawater resistivity at low temperature. However, there are still questions regarding the influence on initial polarization currents on maintenance currents and the output performance of many of the various Al-anode systems with

varying Zn content in under low temperature sea bottom conditions. These and other topics are still the subject of ongoing research efforts. Both field and laboratory studies are in progress to better define cathodic protection requirements for deep water in terms of (1) consumption rates for various anode materials (conventional and high performance), (2) anode efficiency, (3) the influence of initial polarization, (4) service temperature and (5) flow rate.

ACKNOWLEDGMENT

REFERENCES

1. "World Water Depth production Records", Brasil Energy, No. 302, Rio de Janeiro, August 1997.
2. S. Srinivasan, and R. D. Kane, "Prediction of Corrosivity of CO_2/H_2S Production Environments", Corrosion/96, Paper No. 11, NACE International, Denver, CO, March 1996.
3. S. Srinivasan, and R. D. Kane, "Methods of Data Synthesis in a Rule-based Representation for Characterization of Corrosion and Cracking in CRAs", Corrosion 92, Paper No. 267, NACE, April 1992.
4. R.D. Kane, "Hydrogen Embrittlement of Steels", Corrosioneering On-line Newsletter, CLI International, Inc., No. 1 Vol. 1, (Internet - http://www.clihouston.com/hec.html), Houston, Texas, November 1996.
5. I.S. Cole, et.al., "The Stress Corrosion and Corrosion Fatigue Properties of Two High Strength Steels for Tubulars", Engineering Solutions for Corrosion in Oil and Gas Applications, Proceedings of the 2nd NACE International Symposium, Houston, Texas, Nov. 1989.
6. Kaneko, et.al., "Influence of Microstructure on SSC Susceptibility of Low Alloy High Strength Oil Country Tubular Goods", Corrosion, Vol. 45, No. 1, Jan 1989, pp 2-6.
7. M.S. Cayard and R.D. Kane, "Serviceability of 13Cr Tubulars in Oil and Gas Production Environments", Proceedings Eurocorr'97 (Event No. 208), European Federation of Corrosion, Sept. 1997, pp 109-115.
8. R. Schutz , "Recent Developments in Titanium Alloy Application in the Energy Industry", presented at the International Symposium on TMP and Metallurgy of TitaniumAlloys at TMS THERMEC'97, Wollongong, Australia, July 7-11, 1997
9. A.J. Sedricks, "Minimizing Marine Corrosion Problems by Using Advanced Materials", Proceedings of ADVMAT/91, First International Symposium on Environmental Effects on Advanced Materials, NACE International, Houston, Texas, June 1991. p4-1/17.
10. A. Ethridge, Private communication Wellstream, Div. of Dresser, Panama City, FL, Nov. 1997.

11. A.D. Ethridge and M.S. Cayard, "Application of Standard SSC Test Methods for Evaluating Metallic Components of Non-bonded Flexible Pipe", Paper 55, Corrosion/97, NACE International, Houston, TX, March 1997.

12. W.H. Hartt, et. al., "The Influence of Temperature and Exposure Time Upon Calcareous Deposits", Corrosion/86, Paper No. 291, NACE International, Houston, TX, March 1986.

RDK-C/MD/Papers/DeepWater1

TABLE 1 - Stainless Steels, Nickel Alloys and Titanium Alloys

Stainless Steels
Nominal composition, wt%

Designation	Fe	Ni	Cr	Mo	N	Other	Comments
Martensitic SS							
13Cr	Bal	-	12.5	-	-	-	low cost/resists CO_2 corrosion
Super 13Cr*	Bal	5.0	12.5	2.0	-	-	improved corrosion resistance over 13Cr
15Cr	Bal	1.5	14.5	0.5	-	-	improved corrosion resistance over 13Cr
Duplex SS							
18Cr*	Bal	4.5	18.5	2.5	00.7	-	lower cost than 22/25Cr alloy
22Cr	Bal	5.5	22.0	3.0	0.10	-	resists CO_2 and low/mod H_2S
25Cr	Bal	6.0	25.0	3.5	0.15	-	higher performance than 22Cr especially with N and W additions in some alloys
High alloy austenitic SS							
28Cr	Bal	31.0	27.0	3.5	-	-	higher resistance to CO_2, mod H_2S and Cl
254S Mo	Bal	18.0	20.0	6.0	0.20	-	low Ni and Cr content but high Mo and N for pitting resistance
904 L	Bal	25.0	21.0	4.5	-	-	low Ni and Cr content but high Mo and N for pitting resistance
6XN	Bal	24.0	21.0	6.5	0.20	-	low Ni and Cr content but high Mo and N for pitting resistance

Nickel-Base Alloys
Nominal composition, wt%

Designation	Fe	Ni	Cr	Mo	N	Other	Comments
Cold worked							
2535	Bal	38.0	25.0	3.0	-	-	lower nickel content than 825, higher, higher pitting resistance
825	Bal	42.0	21.0	3.0	-	-	good resistance to CO_2/high H_2S and Cl /moderate temperature
G-30	20	Bal	22.0	7.0	-	-	good resistance to CO_2/high H_2S and Cl/high temperature
2550	20	50.0	25.0	6.0	-	2.5W	better resistance than G3 to CO_2/high H_2S and Cl
G-50	17	50.0	20.0	9.0	-	-	better resistance than G3 to CO_2/high H_2S and Cl
C-22	4.0	Bal	21.0	13.5	-	3.0W	alternative to C-276 in some environments
C-276	5.5	Bal	15.0	16.0	-	3.5W	excellent resistance to CO_2/high H_2S and Cl/very high temperature and sulfur
Precipitation hardened							
925	Bal	42.0	21.0	3.0	-	2.0Ti	lower cost than 718, but better pitting resistance
718	Bal	52.0	19.0	3.0	-	1.0Ti/5.0 Cb	good resistance to CO_2/mod H_2S and Cl
725	8.0	Bal	21.0	8.0	-	3.4	better pitting and SCC resistance than 718
625 plus	5.0	Bal	21.0	8.0	-	1.5Ti/3.5 Cb	better pitting and SCC resistance than 718

Titanium Alloys

ASTM Grade	Min. YS ksi (MPa)	Alloy Composition	Comments
2	40 (275)	Unalloyed Ti	Most common C.P. grade
5	120 (828)	Ti-6A1-4V	Common, standard grade
12	50 (345)	Ti-0.3Mo-0.8Ni	Normal interstitials
23	110 (759)	Ti-6A1-4V ELI	0.13% max. O
28	70 (483)	Ti-3A1-2.5V-0.1Ru	0.15% max. O (0.08-0.14%Ru)
29	110 (759)	Ti-6A1-4V-0.1Ru	0.13% max.O (0.08-0.14%Ru)
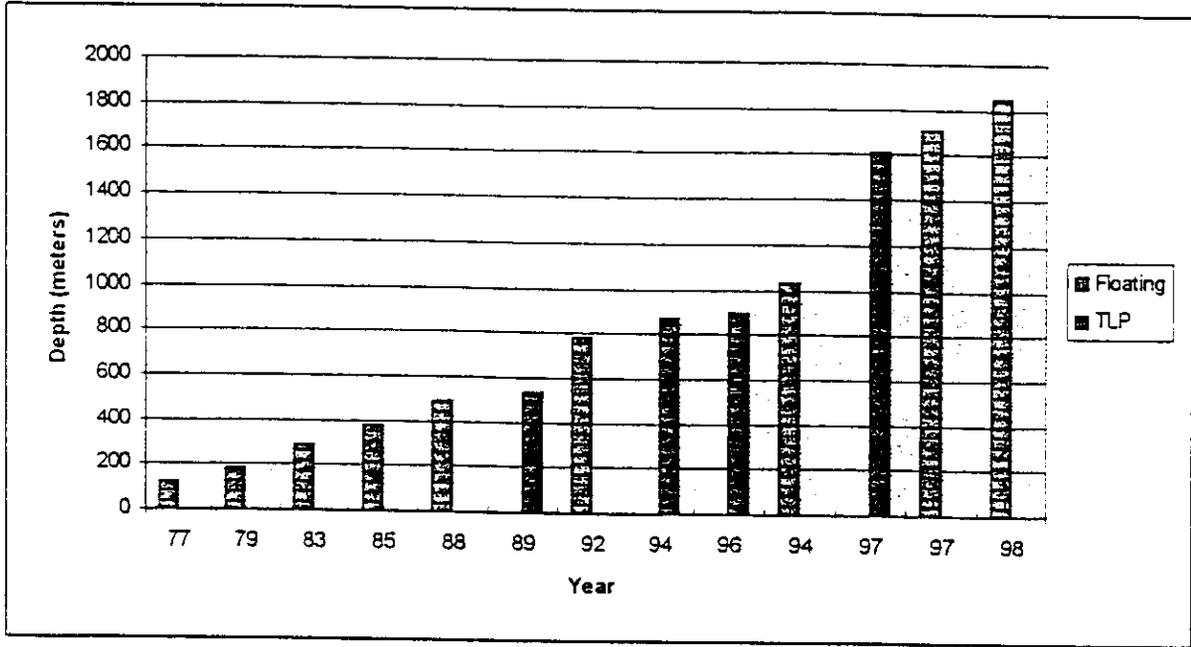
Figure 1 - World water depth production records
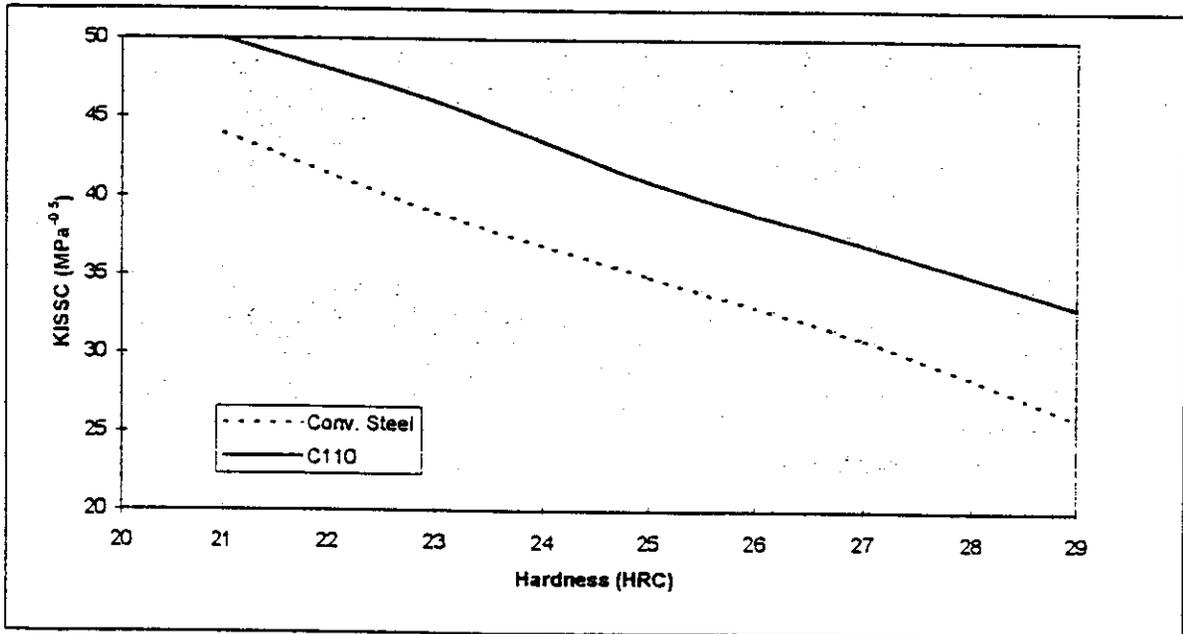
Figure 2 - Hydrogen embrittlement during cathodic charging versus
hardness and hydrogen concentration for high strength steel.
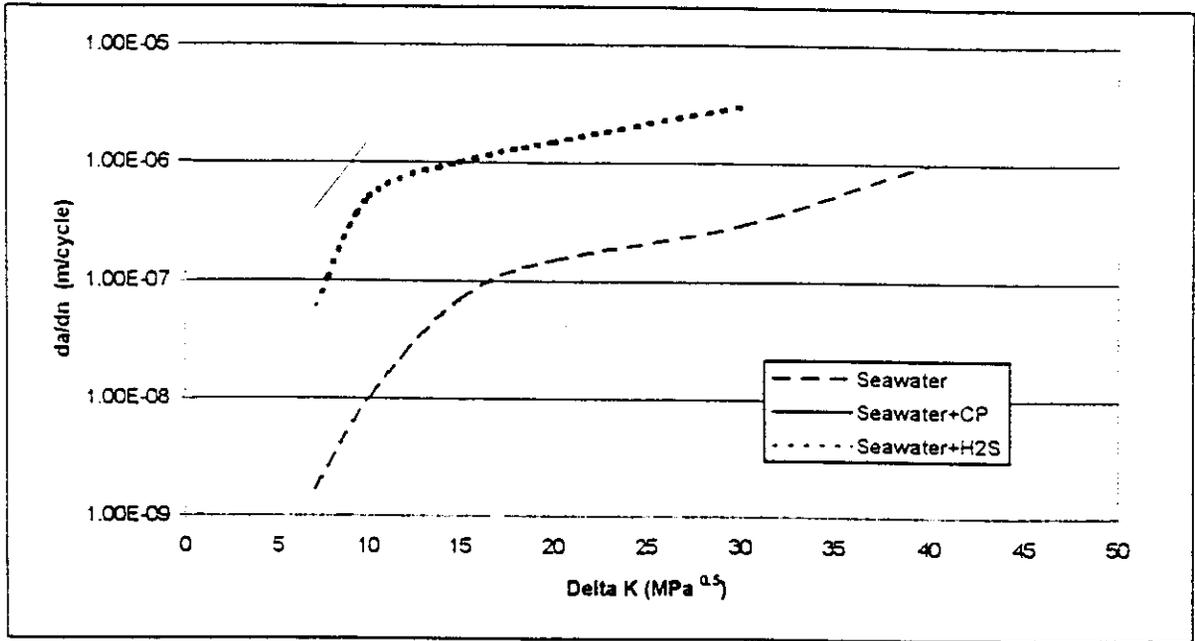
Figure 3 - Fatigue crack growth of high strength steel (HSLA80) in seawater, seawater with cathodic protection (-1.0 V SCE), and H_2S contaminated seawater.
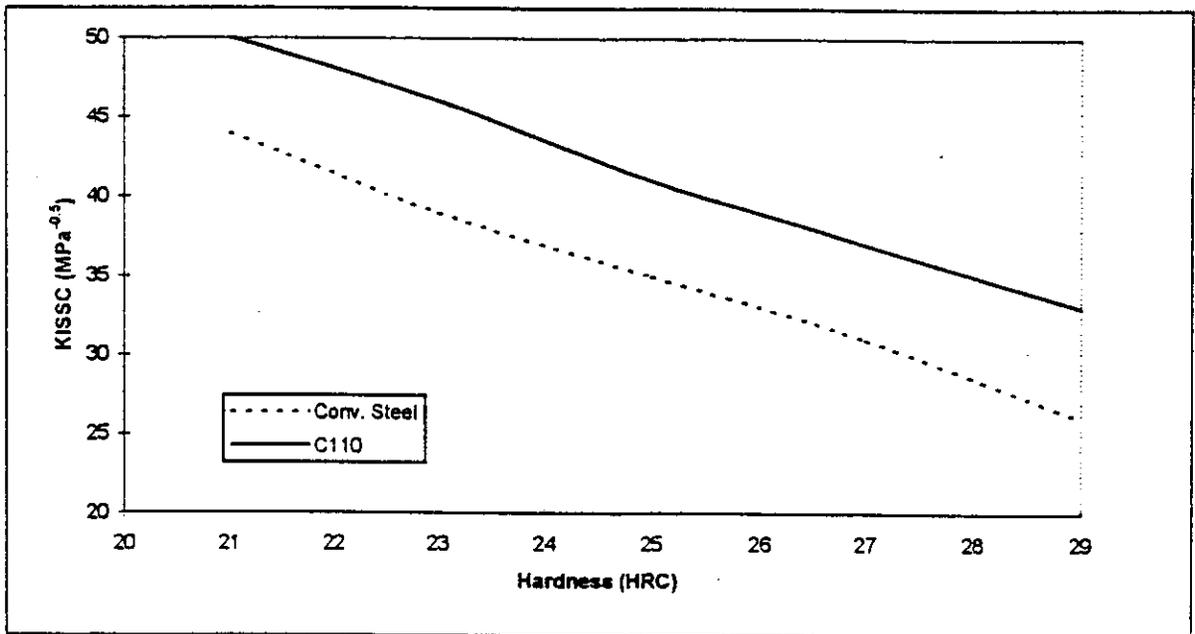
Figure 4 - SSC resistance of C-110 versus conventional high strength casing grade steel.
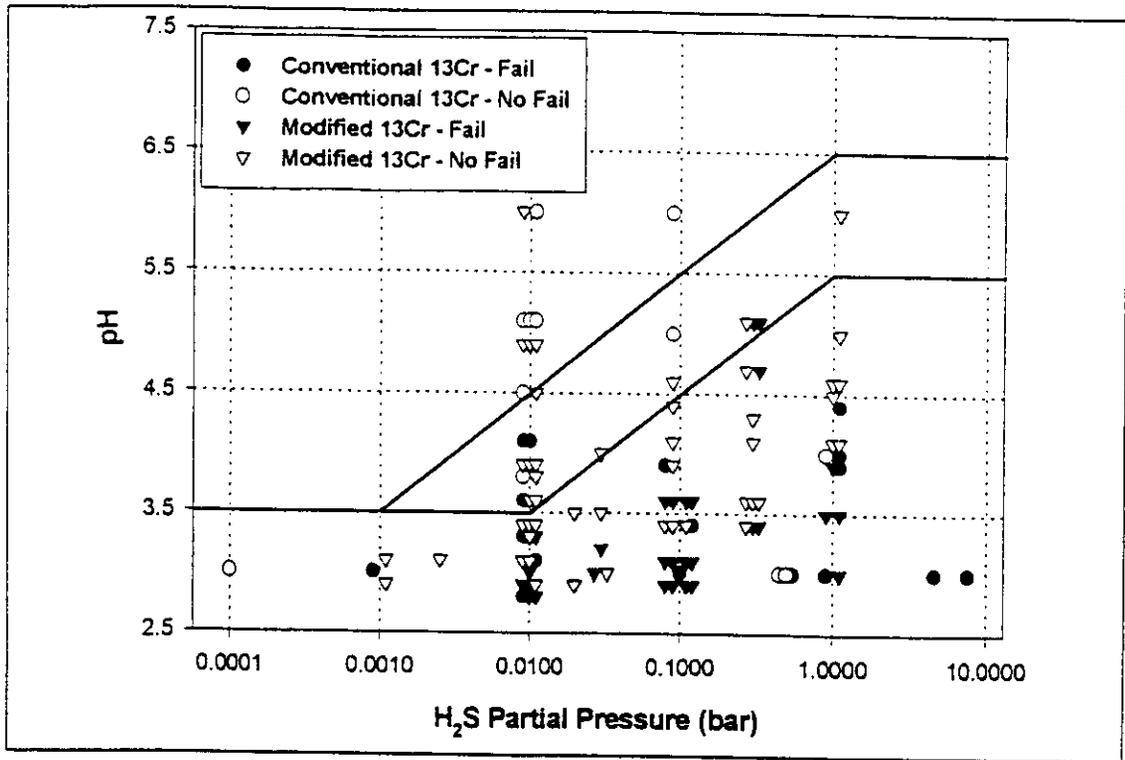
Figure 5 - Data on SSC of 13Cr and Modified 13Cr alloys
versus H_2S partial pressure and pH.
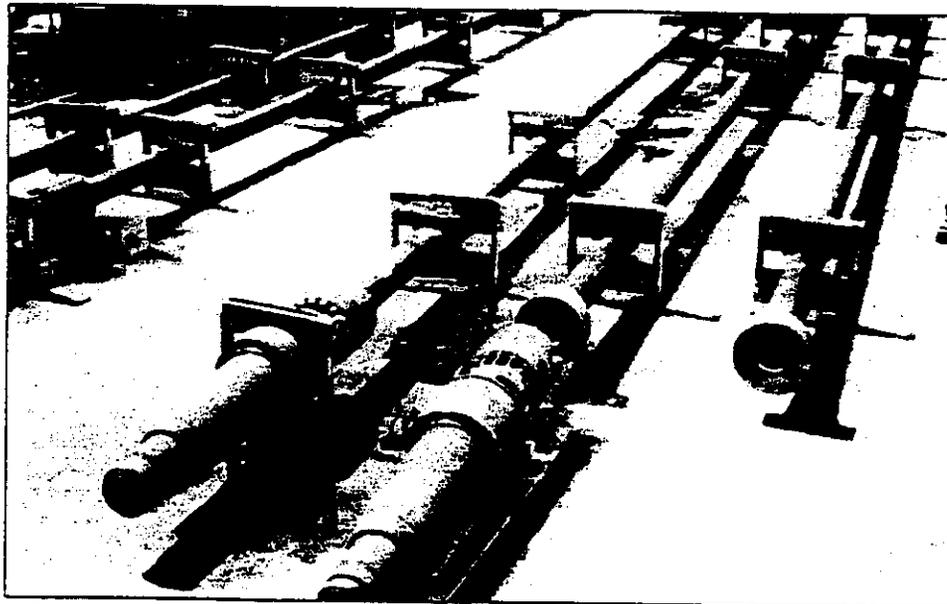
Figure 6 - Grade 23 titanium taper stress joints manufactured for the
Oryx-Neptune Spar Production Riser System, showing flange
connection to steel wellhead tie-back connectors (right side)
(Courtesy of RMI Titanium)
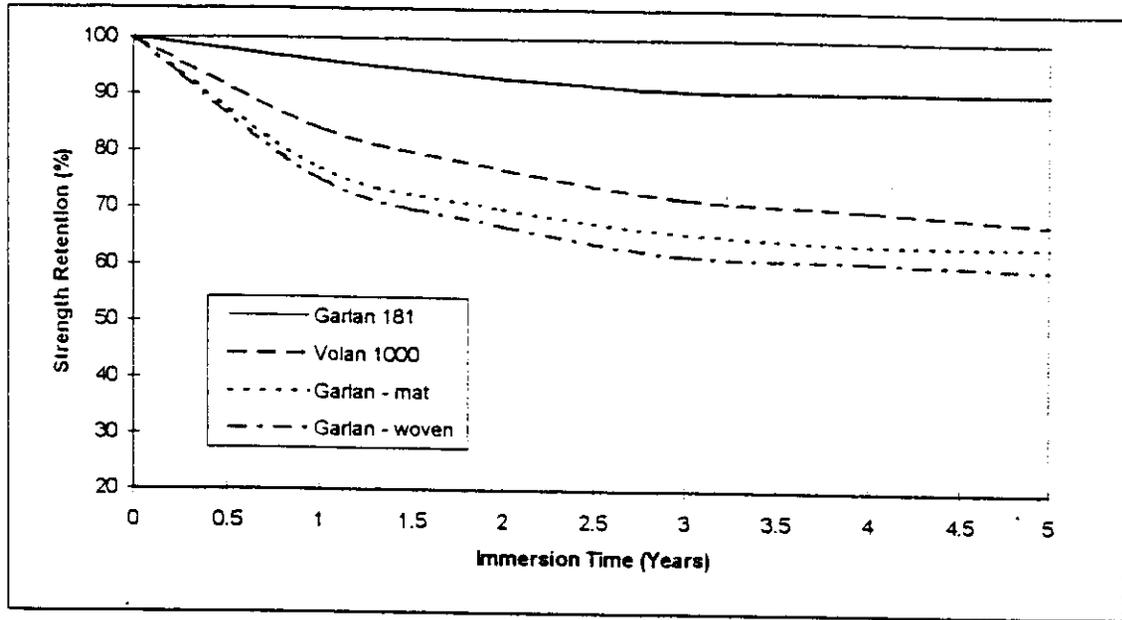
Figure 7 - Strength retention of FRP composites with time due
to moisture absorption during seawater.
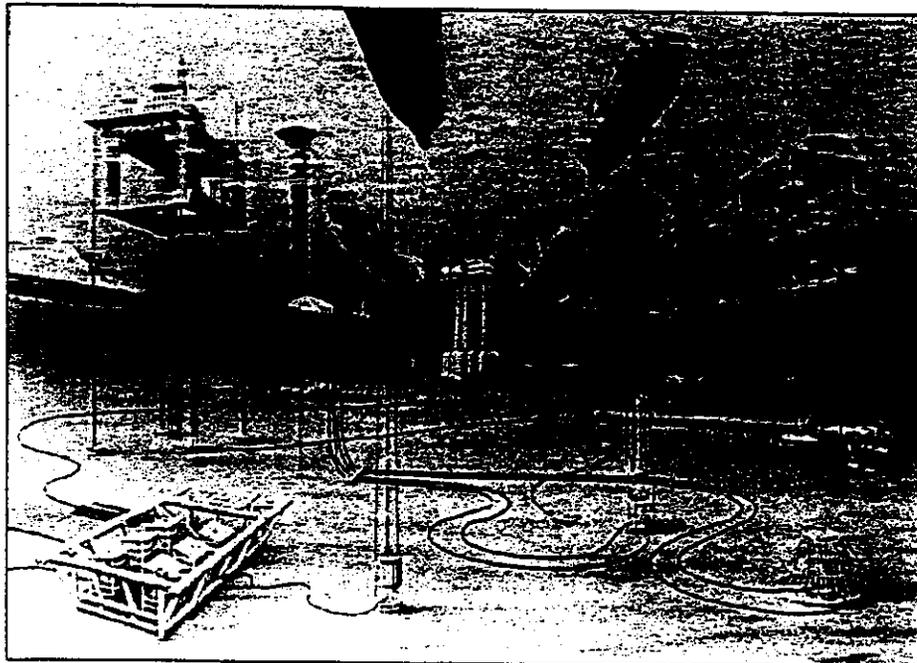
Figure 8 - Various types of offshore systems. (Courtesy of Wellstream)
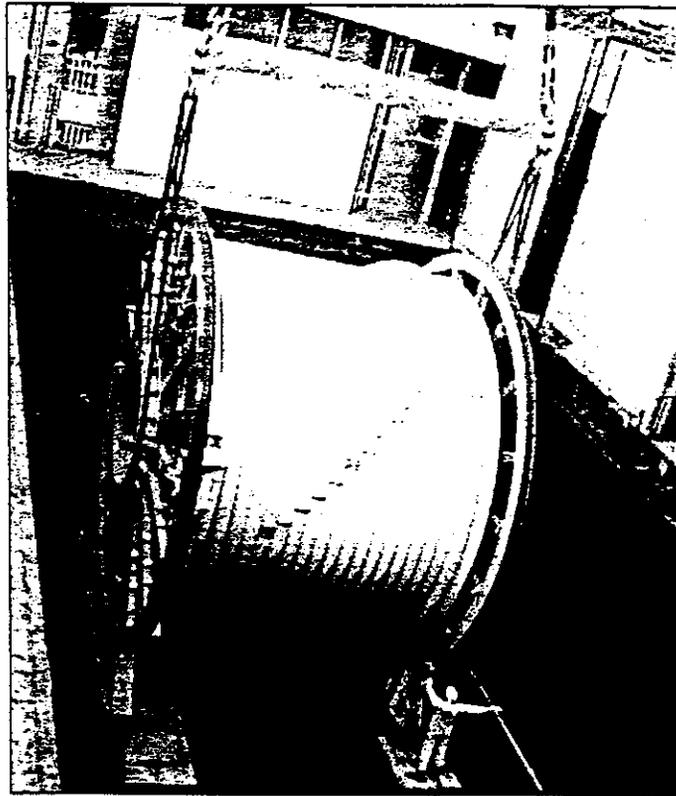
Figure 9 - Spool of flexible pipe. (Courtesy of Wellstream)

EXTERNAL FLUID BARRIER
TENSILE STRENGTH LAYER
ANTI-WEAR LAYER
TENSILE STRENGTH LAYER
ANTI-WEAR LAYER
HOOP STRENGTH LAYER
FLUID BARRIER
COLLAPSE RESISTANT LAYER
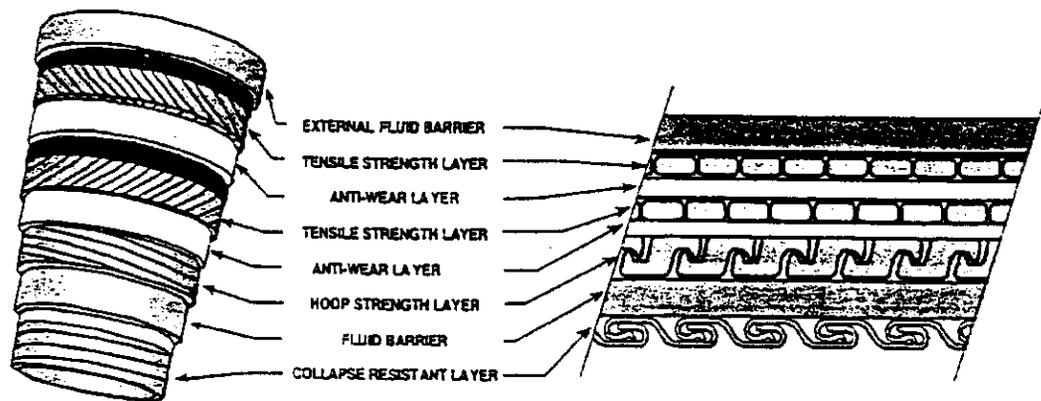
Figure 10 - Typical lay-up of flexible pipe system. (Courtesy of Wellstream).
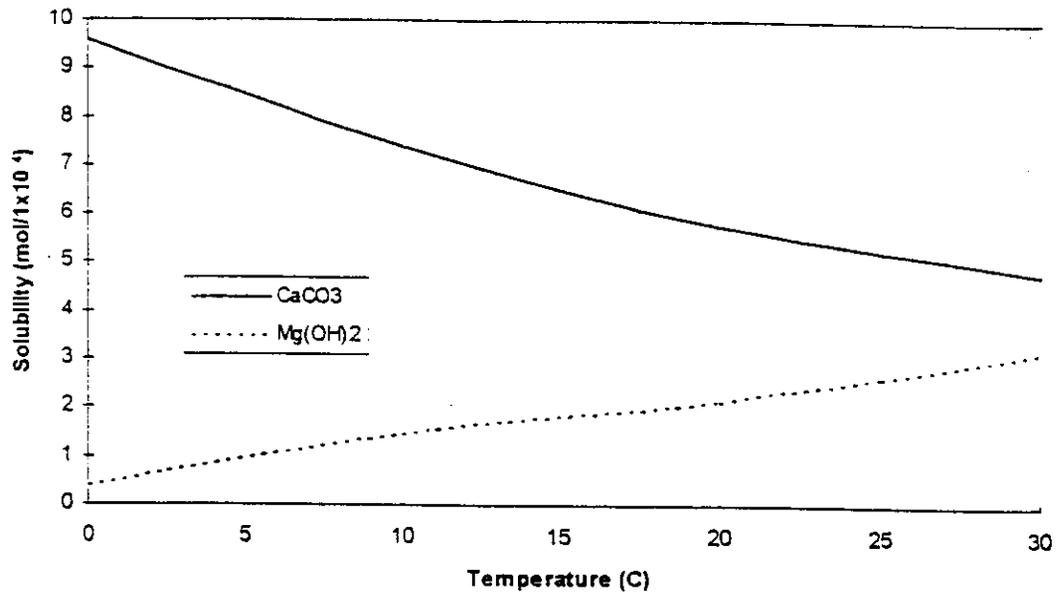
Figure 11 - Variation in $CaCO_3$ and $Mg(OH)_2$ solubility limits with temperature.

Corrosion Protection of Ballast and Cargo Tanks of Crude Oil Tankers

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Abstract

Since 1970 six generations of crude oil tankers both single hull and double hull types have been phased into service in the Chevron Shipping Company fleet. As the owner/operator, Chevron has encountered some corrosion problems in water ballast tanks and cargo oil tanks such as early coating failures, excessive pitting corrosion, accelerated general corrosion, etc. Mitigation strategy and maintenance methodology on how to control tank corrosion throughout the life span of these tankers are discussed.

Practical guidelines for tank coatings to achieve a long coating life of 20 to 25 years are also addressed emphasizing the needs of do-it-right-the-first-time during newbuilding and continuous in-service maintenance of coatings.

Introduction

Corrosion is inevitable in water ballast and cargo tanks of crude oil tankers. The effect of corrosion over a period of time is to reduce material thickness and hence the strength of the structure. Each individual crude oil tanker usually exhibits a unique, but controllable corrosion. Should the corrosion proceed and remain unchecked, a structural failure, with consequent oil spillage, explosion, or loss of ship, could result.

In this paper, experiences in corrosion problems of coated ballast tanks, and both coated and uncoated cargo tanks are presented and mitigation strategy and maintenance methodology are discussed.

In addition, practical guidelines have been developed from lessons learned from past experiences to achieve a long tank coating life of 20 to 25 years.

Coating Failures In Coated Ballast Tanks

Ballast tanks are usually coated to meet classification society requirements. Coating breakdowns are primarily due to poor coating system, poor workmanship and lack of quality control during newbuilding, aging of coatings, and lack of maintenance. Some examples are as follows:

1. Necking was observed at the junctions of horizontal stiffeners and longitudinal bulkhead plating adjacent to heated cargo tanks. Flexing of bulkhead plating due to cyclic loading from heated cargo and water plus an accumulated mixture of mud and water on top of stiffeners had caused the coating breakdown. Lack of safe accessibility to the upper part of double hull wing spaces had hindered coating inspection and repair. Coating failures were hidden until an oil leak occurred at 15 years service. Almost 80% of the longitudinal bulkhead plating was renewed and the entire double hull wing space was reblasted and recoated (see Figure 1).

2. Pinhole blisters and cluster rust were detected at the bottom of double hull spaces. One or a combination of the following could be the causes: grit inclusion, solvent inclusion, salt inclusion and insufficient secondary surface preparation (see Figure 2).

3. Edge peeling was recorded at free edges and rust was noted on hand rails and fittings. Lack of stripe coats and insufficient surface preparation could be the causes (see Figure 3).

4. Large sheet of coating breakdown was noted. Insufficient secondary surface preparation and improper paint application could be the causes (see Figure 4).

5. Edge peeling was observed at air holes and at drain holes. This is due to lack of stripe coats and a coating-unfriendly structural design that inhibits good coating application; the air hole is too close to the edge of the stiffener (see Figure 5).

6. Corrosion was noted at welds and at edges. Lack of stripe coats is the cause of coating breakdowns (see Figure 6).

7. Corrosion perforations were recorded in the deckhead web frames on a 22-year-old tanker. This is due to lack of in-service coating inspection and repair. Accessibility to the deckhead web frames is only available by rafting or staging (see Figure 7).

The integrity of tank coatings depends on continuous in-service inspection and repair. Cost-effective coating repair during voyage in lieu of repair in shipyard becomes feasible with advanced technology of high pressure water and slurry blasting and marginal surface type coatings recently available (see Figure 8).

Improvements Of Accessibility And Coating Practices For Newbuildings

Lessons learned from past coating failures have been incorporated into the design and construction of new generation of double hull tankers (see Figure 9). The improvements are described below:

1. Improved accessibility in wing spaces for inspection and repair
   * Incorporate horizontal stringers at 4 -6 meters interval.
   * Install walkways around the perimeters of wing tank spaces.
   * Install ladder to assist climbing.

2. Improved tank coating practices
   * Implement 1, 2 or 3-cut grinding of free edges.
   * Include two stripe coats for free edges and welds.
   * Use light color coating in double hull spaces.
   * Apply coating-friendly structural design.

Excessive Pitting Corrosion In Bottom Plating Of Uncoated Cargo Tanks

In uncoated bottom plating of cargo tanks, pit densities of 200 to 400 pits per square meter were found in recently built tankers of both single hull (SH) and double Hull (DH) types, and of only 2 to 5 years of age. These tankers were constructed using either conventional high tensile steel (CHT) or Thermo-Mechanically Controlled Process (TMCP) steel (see Figures 10 and 11). The average pitting corrosion rate is 0.6 to 1.5mm per year, but maximum pitting corrosion rates as high as 2.0mm per year have been recorded. Acidity as low as 1.0 to 2.0 pH are measured at the bottom of pits which indicates corrosion is very active inside the pit.

This alarming accelerated pitting corrosion rate is approximately 4 to 5 times greater than normally anticipated and has been diagnosed as due to Microbial Influenced Corrosion (MIC) attack. The presence of MIC attack is indicated by the appearance of pits-within-pits and stairstep-look (see Figures 11 and 12).

Microbial Influenced Corrosion is the combination of normal galvanic corrosion processes and microbial metabolisms. The presence of microbial metabolites generates corrosive environments which promote normal galvanic corrosion at an accelerated rate.

Bacteria test results for 11 tankers indicated that MIC bacteria consortia exist not only in the settled water and sludge at the bottom of cargo tanks, but also in the water droplets in the crude oil itself. The bacteria originate in water, or contaminated crude oil from water injection oil wells, storage tanks and pipelines. The group of bacteria having the greatest corrosive effect on steel, sulfate-reducing bacteria (SRB), was found in concentrations as high as 100,000 to 10,000,000 per milliliter in the settled water (see Figure 13).

Biocide Treatment To Control MIC In Cargo Tanks

A field test of biocide efficacy was carried out in 1995. Initial shock treatment with high dosage of biocide was effective in killing all bacteria in settled water; however, after 2 months of loading/discharging crude oil, the bacteria began to re-grow. After 9 months, the bacteria count was 100 times greater than it was originally (see Figure 14). This proved that a continuous biocide treatment becomes necessary. This also proved that biocide treatment will not be cost-effective in the long run due to the sheer size of the bottom area.

Since the biocide may not penetrate the scale to reach inside the pits, the efficacy of biocide treatment is doubtful. Furthermore, cargo loss due to biocide/treated water weight, inability to dispose of biocide/treated water residuals, and refinery unwillingness to accept treated crude oil are some unfavorable factors concerning the biocide treatment. In addition, handling of toxic biocides by tanker personnel on a frequent and ongoing basis substantially increases safety risk that is unacceptable by the company risk management standards.

In summary, biocide treatment was found to be impractical onboard tankers.

Mitigation Strategy And Maintenance Methodology For Bottom Pits

It can be expected that MIC attacks will continue to occur in cargo tanks. MIC bottom pitting corrosion has two severe consequences if left unchecked:

1. The corrosion pit will become a corrosion hole, and in the case of a single hull tanker, an oil spill may occur. In the case of a double hull tanker, there may be oil leakage into the double hull spaces that may cause an explosion.

2. If dense, deep pits begin to merge, structural strength will be significantly reduced. Steel renewal of bottom plating may become imperative.

Based on past successful pitting inspection and repair of coated bottom plating since 1980 (see Figure 15 that shows well maintained coated bottom plating of a 22 years old tanker), a cost-effective mitigation strategy and maintenance methodology can be employed for the existing uncoated bottom plating, as described below:

1. Blasting and Coating of Bottom Plating
   It should include at least 300mm high of adjacent bottom structural members and be coated with bacteria-resistant pure or modified epoxy coating before the pitting corrosion poses the

unacceptable risk of an oil spill, or requires an unsatisfactory amount of steel renewal at the next scheduled periodic overhaul. The epoxy coating will provide a barrier that prevents bacteria from contacting the bottom plating directly. However, since the bacteria could still reach the bottom plating through any coating breakdown areas, the coating must be regularly inspected and maintained and any pits in the coated bottom plating must be repaired. Although pitting inspection and repair must still be performed for the coated bottom plating, only a finite number of pits must be dealt with, rather than the nearly infinite number to be found in uncoated bottom plating.

2. Implementation of an Enhanced Pitting Inspection and Repair Program.
   The condition of bottom pitting corrosion is monitored at specific intervals. Any pits discovered are to be repaired according to specified criteria that meet each individual tanker design scantling and operation requirements. This will effectively eliminate the deep pits. This enhanced program is also applicable to uncoated bottom plating before coating is done (see Figure 16). Pitting inspection and repair can be performed during voyage or in the shipyard. A typical program for an assumed 15.0mm thickness of bottom plate and a 60-month periodic overhaul interval is in Appendix A.

For newbuildings, the entire bottom plating in cargo tanks should be coated with two coats of pure or modified epoxy of lighter color.

Accelerated General Corrosion In Vaporspaces Of Uncoated Cargo Tanks

Excessive steel scale was found falling off from deckhead structures in uncoated cargo tanks, particularly in the forward part of cargo areas adjacent to the Fore Peak Tank. The general corrosion rate of deck plating at amidships was 0.02 to 0.1mm per year and that is within normally anticipated range. However the general corrosion rate at the forward part of cargo areas was 0.1 to 0.25 mm per year and that is approximately 2 to 3 times greater than normally anticipated (see Figures 17 and 18).

Since the design thickness of deck plating is determined primarily to meet hull girder bending moment requirements, the thickness at both the forward and after ends of a ship have been tapered thinner than that at amidships. For example, a typical 150,000 dwt Suezmax tanker has 15.0 to 17.0mm deck plate thickness amidships, but only 12.5mm in the forward end of ship.

The combination of higher general corrosion rate and thinner deck plate thickness in the forward part of cargo areas gives cause for serious concern. Therefore an investigation program was initiated in 1995 to study the vaporspace corrosion and to develop the mitigation strategy and maintenance methodology.

Cargo Tank Vaporspace Corrosion Investigation

The vapor space corrosion investigation program consisted of six parts:

1. Corrosion probe and coupon installation on four tankers.

2. Cargo tank temperature profile monitoring on five tankers.

3. Vaporspace gas and water condensate analysis on 4 tankers.

4. Laboratory simulation - bottle tests (in conjunction with MIC investigation).

5. Paint bacteria resistance tests (in conjunction with MIC investigation).

6. Continuous thickness measurements for vapor space corrosion rate monitoring.

The following sections present the investigation results and discussions on the findings.

Corrosion Probe And Coupon

Since corrosion probes and coupons are bolted to structural members, they are not affected by the ship bending stress, motions and vibration (see Figure 19). The correlation of corrosion rates between probe and coupon is good, but the correlation with the actual thickness measurements (gaugings) of deck plates and deck longitudinals is poor (see Figure 20). Corrosion probes and coupons can provide the real time corrosion process trend but can not provide the actual corrosion rate of the hosting structural member.

Thickness gaugings and pit depth measurements are the only practical methods to obtain the actual in-service corrosion rates of structural members.

Cargo Tank Temperature Profile

The temperature gradient inside the cargo tank is affected by cargo heating and outside ambient temperature more than the sea temperature for single hull tankers. For double hull tankers, the double hull space surrounding the cargo tank seems to have no direct effect to the cargo tank temperature (see Figure 21).

Since cargo tanks are not insulated, it is impractical to control the temperature inside the cargo tanks.

Vaporspace Gas And Water Condensate Analysis

Gas in vaporspace is a mixture of inert gas, water vapor and oil vapors. Results from measurements of 4 tankers indicated high contents of carbon dioxide (11%) and water vapor (0.46 gram/liter gas). Oxygen content is 5 to- 6 % and nitrogen content is 82%. Depending on the type of crude oil, hydrogen sulfide content could be more than 600 ppm (see Figure 22).

The presence of water condensate is indicated by the appearance of widespread, small, round and shallow pits at the underneath side of deck plating. Vaporspace water condensate could be very acidic and has been recorded as low as pH 1.00.

Inert gas quality could be controlled, but water vapor (from deck water seal and oil itself) and oil vapors are uncontrollable.

Laboratory Simulation - Bottle Tests

Five test bottles containing crude oil and synthetic sea water, inert gas (four bottles) and nitrogen gas (one bottle) were tested for 5 months in room temperature (230 C, two bottles) and elevated temperature at 400 C (three bottles). Four bottles had also inoculated with SRB (see Figure 23).

Four bottles had two types of steel coupons (mild steel and TMCP steel) in the bottom of the bottle and its vaporspace. Corrosion probe, temperature/humidity probe and oxygen probe were also included (see Figure 24).

The bottle tests have simply confirmed already known phenomena:

1. 5-month-only test period reveals only the beginning of the corrosion process.

2. No evidence of microbial organisms is present in the vaporspace.

3. Evidence of Microbial Influenced Corrosion shows in color change of settled water that turns black (compare bottles A and B in Figure 23).

4. Corrosion rate for coupon is derived from weight loss which includes pitting corrosion loss. Therefore it is not the true corrosion rate of surface layer loss over time. This has reconfirmed that actual thickness measurements are necessary (see Figure 25).

5. Pits are randomly formed regardless of type of steel (see Figures 26 to 29).

6. Pitting corrosion in bottom coupon revealed the same patterns as the cargo tank bottom.

7. Inherent surface roughness and inclusion of micro-pits could affect initial formation of pits in bottom and vaporspace.

8. Temperature effect is evidenced - the corrosion rate at 400C is twice that at 230C.

Paint Bacteria Resistance Tests

In cooperation with the International Paint, bacteria resistance tests were carried out for four different epoxy paints coated on coupons that submerged in SRB inoculated mixture of oil and sea water. After a 40-day test, it has confirmed that pure and modified epoxy coatings have good bacteria resistance.

Continuous In-Service Thickness Monitoring For Vaporspace

Since the corrosion in cargo oil tanks is a comparably slow process, its impact on structural strength and effect on oil spill will take years to develop. Due to different trading routes and cargo types carried, each individual tanker has its own unique pattern of corrosion. Therefore continuous in-service thickness monitoring becomes a necessary part of the lifetime corrosion control program. Thickness measurements for selected structural members in selected cargo tanks at 30-month intervals can normally provide an adequate corrosion database for developing the mitigation strategy and maintenance methodology for corrosion. Results of Thickness gaugings are analyzed statistically for corrosion rate determination (see Figure 18).

Other Findings

Several observations from this investigation program are worthwhile to be discussed:

1. Duration of voyage has no direct effect on bottom pitting and vaporspace corrosion. Rather, the microbial activity of MIC bacteria, temperature inside the cargo tank, inert gas quality and cargo vapor quality are the most important influencing factors.

2. Crude oil washing (COW) and oil sediment have no direct effect on bottom pitting corrosion.

3. COW has no direct effect on vaporspace corrosion. Rather, the flexing and vibration of structures have greater impacts. The excessive corrosion of deck plating in the forward part of cargo areas could be caused by ship motions and the use of anchor windlass.

4. TMCP (Thermo-Mechanically Controlled Process) steel is widely used in today shipbuilding. Concern has been raised regarding the corrosion characteristics of TMCP steel. From the bottle tests and the actual inspections of cargo tanks, interesting facts and observations that have yet to be investigated further are as follows:
    a. TMCP steel shows no difference with conventional mild steel or high tensile steel in pitting corrosion rate in bottom plating (see Figure 30).
    b. TMCP steel could be initially more susceptible to localized pitting corrosion due to the initial roughness of steel surface; perhaps due to the accelerated water spray cooling and hot press during rolling process.
    c. TMCP steel could have higher density of complex, large face, stairstep type pit possibly due to the peeling effect of thinner micro-layers between pearlite and ferrite during the corrosion process.
    d. TMCP steel could eventually have higher general corrosion rate due to the merging of complex, large face, stairstep type pits.

Mitigation Strategy And Maintenance Methodology For Vaporspace Corrosion

For existing tankers, coating is the only practical method to mitigate the vaporspace corrosion. However when and to what extent (which tanks have to be coated) must be tailored for each tanker depending on the actual in-service corrosion monitoring results. The forward part of cargo areas where the corrosion rate is higher and plate thickness is thinner should be coated first. The coating should extend down from the deck plate to cover deck longitudinals and other underdeck structural members at least 1.0 meter down.

For newbuildings, the entire vaporspace in cargo tanks should be coated with two coats of pure or modified epoxy of light color. Another alternative is to increase scantlings of underdeck structural members to provide additional thickness for corrosion wastage.

Guidelines For Tank Coatings

From the past experiences learned, we believe that a tank coating system could achieve a long life of 20 to 25 years if it is done correctly during newbuilding and properly maintained afterward. The following are practical guidelines for tank coatings:

1. Do-it-right-the-first-time during newbuilding
    a. Apply coating-friendly structural design.
    b. Provide proper (inspection-friendly) accessibility in wing spaces.
    c. Select a good coating system:
        *   Correct paint of light color for intended service.
        *   Two coats of 300 to 350 microns total dry film thickness.
        *   Two stripe coats at welds and free edges, 75 microns for each stripe coat.
        *   Grinding of free edges such as 1, 2 or 3-cut grinding, or 1.0 - 2.0mm radius round corner.
        *   Back-up zinc anodes in ballast tanks.
    d. Select a newbuilding yard that has good steel and coating facilities:
        *   Enclosed steel fabrication shops.
        *   Enclosed blasting shops.
        *   Enclosed painting shops.
    e. Apply good workmanship
        *   Use of clean, correct size and type of grit.
        *   Grit blasting for secondary surface preparation.
        *   Removal of soluble salt contaminants.
        *   Removal of oil and grease.
        *   Removal of weld spatters.

- * Thorough cleaning before painting.
- * Proper temperature control.
- * Proper humidity control.
- * Proper paint handling, mixing and spray.
- * Proper coating thickness per application.
- * Proper ventilation.
- * Proper curing/drying time.
- * Proper overcoating time.

  f. Perform diligent inspection and quality control
  - * Shipyard inspector, coating manufacturer inspector and owner inspector should form a team and perform the quality control diligently to ensure that all agreed painting procedures are being followed. Especially, the owner inspector should realize that subsequent costly steel renewal and coating repair would be needed during the vessel life if quality assurance failed during newbuilding.
  - * Must carry out mandatory inspection for
    - (a) Initial steel plate shop blasting and primer application (by periodic auditing).
    - (b) Secondary surface preparation.
    - (c) First coat and stripe coat.
    - (d) Second coat and stripe coat.
    - (e) Dry film thickness measurement.
    - (f) Coating holiday test.
    - (g) Coating pulling test.
    - (h) Coating remedy.

2. Implementing a continuous in-service coating maintenance program.
   a. Coating inspection and repair during voyage at sea that includes repair of coating breakdown areas, repair of bottom pits and installation of back up anodes.
   b. Coating inspection and repair in a repair shipyard that includes repair of coating breakdown areas, blasting and coating of originally uncoated areas and repair of bottom pits and installation of back up anodes.

Conclusions

Corrosion in ballast and cargo tanks can be mitigated by tank coatings.

Lessons learned from past experiences should be applied to the next generation of tankers during newbuilding such as applying coating-friendly structural design and providing inspection-friendly permanent girders, walkways and ladders, and coating of bottom plating and vaporspaces in cargo tanks.

Long tank coating life of 20 to 25 years can be achieved by:

1. Do-it-right-the-first-time during newbuilding.

2. Implementing a continuous in-service maintenance program.

3. Being aware of Microbial Influence Corrosion (MIC).

Acknowledgments

References

1. "Condition Evaluation and Maintenance of Tanker Structures," Tanker Structure Cooperative Forum, May, 1992.

2. "Guidelines for Inspection and Maintenance of Double Hull Tanker Structures," Tanker Structure Cooperative Forum, May, 1995.

3. "Corrosion and Tank Coating Maintenance of Recently Built and Aging Oil Tankers," ASTM/ABS Coatings for Ship and Offshore Seminar and Workshop, December, 1995.

4. Corrosion/97 Paper No. 535 "Microbial Influenced Corrosion in Cargo Oil Tanks of Crude Oil Tankers," NACE International, March, 1997.

5. "Guidance Manual for Tanker Structures," Tanker Structure Cooperative Forum, June, 1997.

6. "Factors Influencing Accelerated Corrosion of Cargo Oil Tanks," OCIMF Information paper, September, 1997.

Appendix A

Enhanced Pitting Inspection and Repair Program

In this program, the condition of bottom pitting corrosion is monitored at specific intervals and any pits discovered are repaired according to specified criteria which meet each individual crude oil tanker operational requirements. This effectively eliminates the deep pits which may become corrosion holes if left unchecked. For example, criteria as specified below are for 15.0mm thickness bottom plate and a 60-month periodic overhaul interval.

The program includes the following procedures:

1. Tanker personnel perform pit inspections and repairs at 15-month intervals, in conjunction with regular tank inspection and maintenance programs.

2. Outside contractors are hired to perform pit inspections and repairs at 30-month intervals, in conjunction with mid-period tank condition assessment inspections and the Intermediate Hull Survey by the classification society.

3. During the periodic overhaul in shipyard (at 60-month intervals), outside contractors perform thorough pit inspections and repairs.

4. Pit repair criteria for uncoated bottom plating:
   a) During voyage
      i)   If pit is less than 3.0mm deep, no repair is required.
      ii) If pit is between 3.0 and 5.0mm deep, pit is to be blasted and filled with white color pit filler (see Figure 15).
      iii) If pit is greater than 5.0mm deep, pit is to be blasted and filled with red-colored pit filler, then welded at the next periodic overhaul (see Figure 16).
      iv) If less than 6.0mm plate thickness remains underneath pit, a strongback patch is to be installed after blasting and filling pit with red-colored pit filler.
   b) Periodic overhaul in shipyard
      i)   If pit is less than 3.0mm deep, no repair is required.
      ii) If pit is between 3.0 and 5.0mm deep, pit is to be blasted and filled with white-colored pit filler.
      iii) If pit is greater than 5.0mm deep, pit is to be welded, blasted and filled with white-colored filler.

5. Pit repair criteria for coated bottom plating:
   a) During voyage
      i)   If pit is less than 3.0mm deep, no repair is required.
      ii) If pit is between 3.0 and 5.0mm pit is to be blasted and filled with white-colored pit filler.
      iii) If pit is greater than 5.0mm deep, pit is to be blasted and filled with red-colored pit filler, then welded at the next periodic overhaul (see Figure 16).
      iv) If less than 6.0mm plate thickness remains underneath pit, a strongback patch is to be installed after blasting and filling pit with red-colored pit filler.
   b) Periodic overhaul in shipyard
      i)   All pits must be repaired regardless of depth.
      ii) If pit is less than 5.0mm deep, pit is to be blasted and filled with white-colored pit filler.
      iii) If pit is greater than 5.0mm deep, pit is to be welded, blasted and filled with white-colored filler.

6. Other general guidelines for pitting repair are found in Table 3.2 of the "Guidance Manual for Tanker Structures (Reference 5).

Working Group Reports

Corrosion Protection of Deepwater Subsea Structures and Pipes
R.T. Hill and M. Karayaka, Aker Maritime, Inc.

Corrosion Control for Ship Structures
P. Rynn and W. Hanzalek, American Bureau of Shipping
J. Kelly, A. Nobel, and C. Bowles, Naval Surface Warfare Center, Carderock
Division

Corrosion in Floating Structures
B. Espelid and E.Tore Moe, Det Norske Veritas

Corrosion Protection of Fixed Offshore Structures
R.D. Holdsworth, Risk, Reliability and Safety Engineering
D.W. Townley, Chevron Research and Technology Company

Corrosion in Pipelines
R.W. Revie, CANMET Materials Technology Laboratory
R.D. Huriaux, U.K. Office of Pipeline Safety

Materials Status and Developments for Oil and Gas Industry Offshore Topside
T. Havn, Aker Maritime, Stavanger
J. Kolts and M. Salama, Conoco, Inc.
R.N. Tuttle, Corupdate, Inc.

Corrosion Control in Ports and Harbors
M. Eskijian, Marine Facilities Division
T. Spencer, Blaylock Engineering Group
D. Polly, NFESC
B. Gerwick, Ben Gerwick, Inc.
R. Heffron, Han-Padron Associates

Corrosion Protection of Deepwater Subsea Structures and Pipes

R. T. Hill and Metin Karayaka
Aker Maritime, Inc.

1. Introduction

The exploration of deep and ultra deepwater oil and gas reservoirs has initiated the development of subsea production systems as stand alone operations, thereby eliminating the need for surface production units. Subsea separation, multiphase boosting pumps, and sea bottom raw water injection systems are just a few of the technologies being used for water depths in excess of 1,000 meters. The lack of infrastructure has also raised the possibility of subsea storage to facilitate direct offloading to shuttle tankers or FSO buffer units.

Corrosion protection of the equipment and hardware associated with the emerging subsea systems as well as more conventional production trees, manifolds, templates, jumpers, and auxiliary piping is a major concern. Deepwater subsea equipment and processing technology consists of a multitude of components manufactured from different materials. Corrosion protection philosophy of these complicated systems needs to consider numerous issues:

1) Deepwater subsea equipment may have material, electrical, and geometric discontinuities. Corrosion compatible materials need to be used in the design.
2) Intervention in the form of repair and/or replacement can be costly as well as result in interrupted production. Therefore, the system needs to be designed for minimal maintenance with a very low risk allowance in the design.
3) A complicated subsea system may have numerous failure points. Therefore, attention to detail is required.
4) Corrosion protection in the form of coatings, cathodic protection, and material selection will be required to ensure a high degree of field reliability. A combination of all of these methods may be required.
5) Corrosion, flow assurance, and performance requirements need to be integrated to design an optimal subsea system.
6) The overall systems approach that takes into account interaction between materials and the operating parameters of the total system.

2. Corrosion Mechanisms

Corrosion mechanisms most frequent to subsea structures are general corrosion, pitting, crevice corrosion, galvanic corrosion, and under certain circumstances, corrosion fatigue, hydrogen embrittlement, and stress corrosion cracking. Depending on the operation and design requirements, several of these mechanisms may simultaneously operate to govern the corrosion performance of deepwater subsea equipment and facilities.

The following factors influence the corrosion mechanisms of the subsea systems:

Temperature: Most of the subsea facilities are designed to operate at elevated temperatures due to conditions of the produced fluids and flow assurance requirements. Elevated temperatures effect all of the corrosion mechanisms. The kinetics of activation and diffusion controlled reactions increase with increasing temperature. Formation of oxide scales is also effected by the high temperatures, which may prevent or accelerate the corrosive attack.

Corrosive attack on the internal equipment surfaces depends on the fluid content which requires understanding of the compatibility of the produced fluids with the equipment material throughout the lifetime of the subsea system at all range of operating temperatures. Increase in temperature also effects the external corrosion mechanisms. Elevated temperature of the exterior surfaces promotes marine growth and biofouling, thereby accelerating pitting corrosion, microbiological corrosion, and underdeposit corrosion damage.

Subsea equipment and facilities may need to be insulated to satisfy flow assurance requirements, which brings about a unique set of conditions; wherein conventional cathodic protection may not be effective and the use of corrosion resistant alloys or aluminum flame spray coatings may be required.

Seawater temperatures in deep water tend to be lower than that previously experienced. Resulting in an additional set(s) of parameters to evaluate during startup or idle operation, which vary from the normal operating conditions. The effects of temperature cycles will effect the kinetics of corrosion mechanism and should not be ignored as to their impact on biofouling or marine growth.

Material selection: Subsea equipment and facilities consist of numerous components. Depending on the selected material different corrosion mechanisms can be activated. Typically, the structural elements are selected to resist the marine attack and cathodic corrosion, whereas, fluid carrying components are selected based on the corrosion requirements of the contained fluid.

Oxygen content: Seawater oxygen content decreases with increasing water depth, therefore, some of the corrosion mechanism may be expected to decelerate due to lack of oxygen, especially for deepwater applications. However, deepwater currents may replenish the oxygen depleted seawater and increase availability of oxygen at the equipment surface. The presence of fresh oxygen at the equipment surface greatly influences cathodic reaction kinetics. Furthermore, at deepwater the partial pressure of the oxygen is higher.

Biological Activity: The biological activity decrease with increasing water depth. However, marine organisms still exist in deepwater and marine growth and biofouling should be expected.

pH: As pressure is increased, pH is reduced according to thermodynamic considerations. Thus, at great depths, there is less tendency for formation of the protective carbonate type scales.
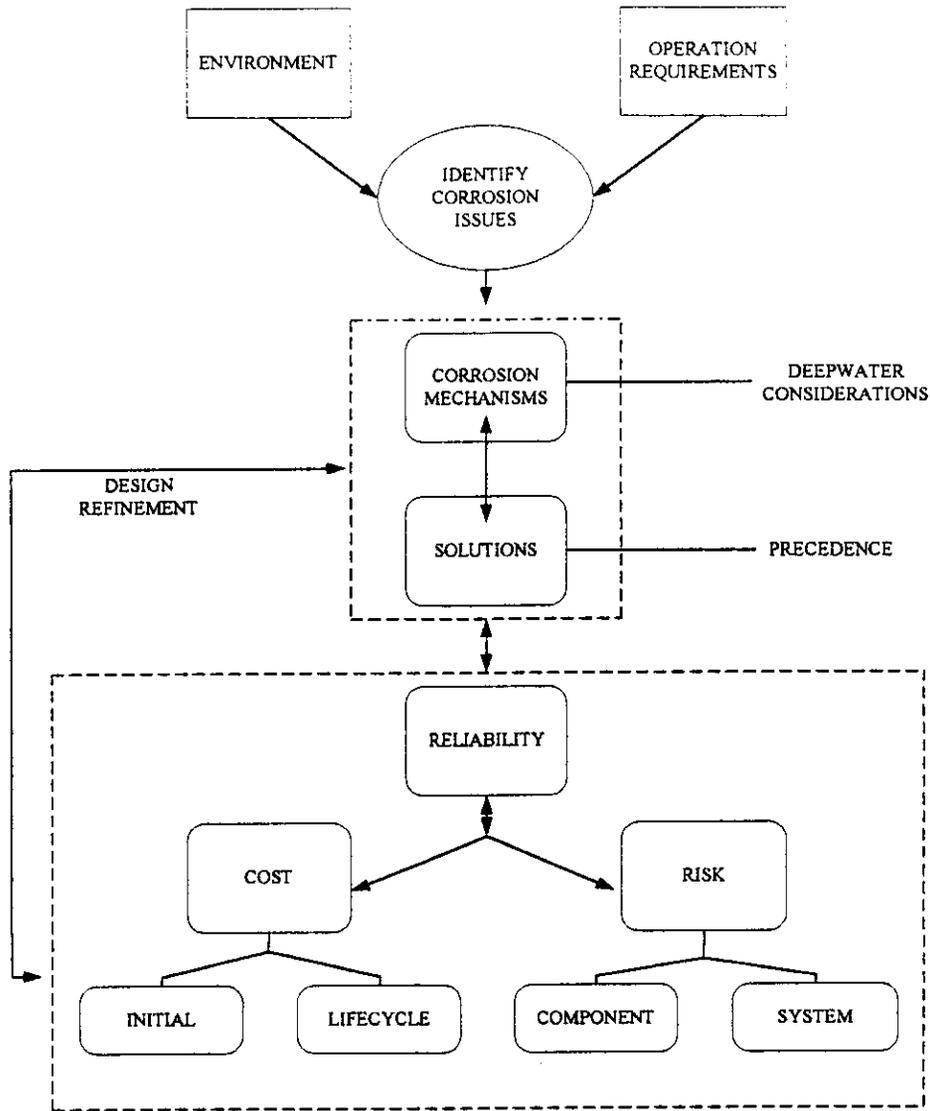
Figure 1: Design Philosophy for corrosion protection of deepwater subsea systems.

3. Corrosion Design Approach

A corrosion protection design philosophy for deepwater subsea equipment is outlined in Figure 1. At the onset of optimal subsea system design, the corrosion issues need to be identified based on operation and environment requirements. After determining potential corrosion issues and associated corrosion mechanisms, the corrosion protection methods need to be established by

considering flow assurance, strength, and performance requirements as well as corrosion requirements.

The balance between the cost and risk of the selected corrosion protection method plays a critical role in finalization of the subsea system design. With high initial investment, minimal maintenance subsea systems can be designed and system reliability can be significantly increased. Another approach is to allow repair and maintenance through the lifetime of the subsea system. For deepwater applications maintenance and repair operations are considerably higher than the shallow water applications. Therefore, both approaches may prohibit economic feasibility of subsea system development. The designer needs to look at the overall system and not focus on an individual piece or sub-component, which supports the involvement of the corrosion engineer in the initial concept development.

Abandonment of subsea production system should be incorporated in the corrosion design to facilitate a cost-effective removal of equipment. Just as with the installation and maintenance cost being high for deep water, also are the costs of removal. Therefore items that were not considered essential in the removal of equipment for shallow water, now can become critical, for example: lifting lugs, ROV control points, structural frames

4. Subsea Production Systems

In this white paper the subsea production system is defined as all equipment and hardware located above the mudline and extending to the pipeline end manifold (PLEM). Corrosion issues related to the tie-back flowlines and/or infield flowline systems are not included in the discussion. In this section corrosion issues related to large subsea components are discussed. These components should be expected to interact with the seawater as well as drilling mud and soil. It should also be noted that subcomponents of this large equipment, such as fasteners, connectors, hydraulic and electrical connectors, and small tubing, are essential in the design..

4.1. Wellhead / Production Tree

The wellhead and production trees integrate the wellbore completion with the seabed equipment and hardware, thereby controlling the production flow through a series of valving arrangements. Horizontal and vertical wellhead and production tree assemblies are shown in Figures 2 and 3, respectively.

Wellheads are designed to be an integral part of the surface casing, such that the corrosion protection is essential. Materials of construction are forged alloy steels. Production trees are made-up of a number of valving arrangements that not only facilitate production flow but also assist in well control. Although most valve body materials are low alloy steels; martensitic forged grade stainless alloy (AISI 410) has also been used. Corrosion protection is normally provided using marine coatings and cathodic protection in the form of sacrificial anodes. The need to minimize heat loss in the production flow requires insulation of production trees. In providing corrosion protection to insulated production trees sacrificial anodes are used, however, the electrical path still needs to be maintained between the valve and the anodes. The corrosion protection requirements should be included in the thermal insulation design.

Debris
Cap
Internal Tree Cap
Production
Valves
Crown Plug
Production
Choke
Annulus Valves
Tree Spool
Body
Production
Flow Line
Connector
Annulus
Flowline
Connector
Tree Connector
Production Guide Base
Intervention Funnel
Wellhead

CAP
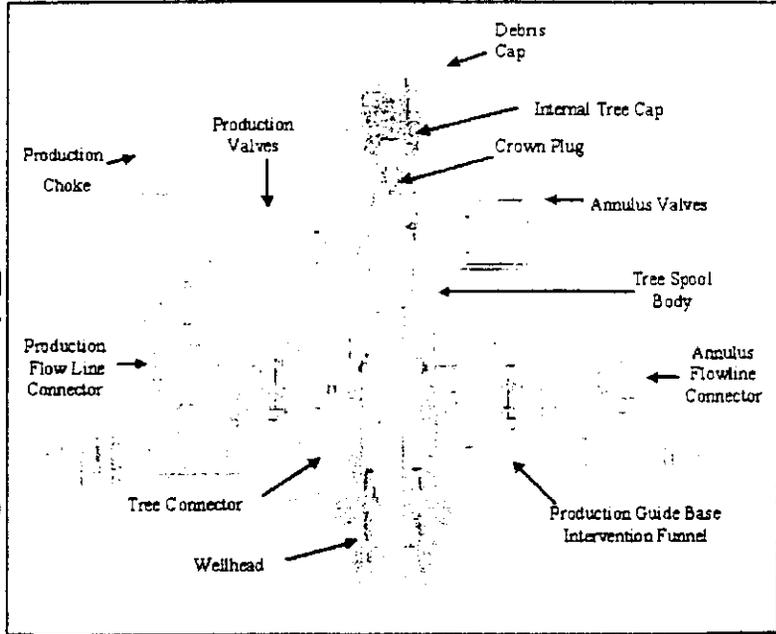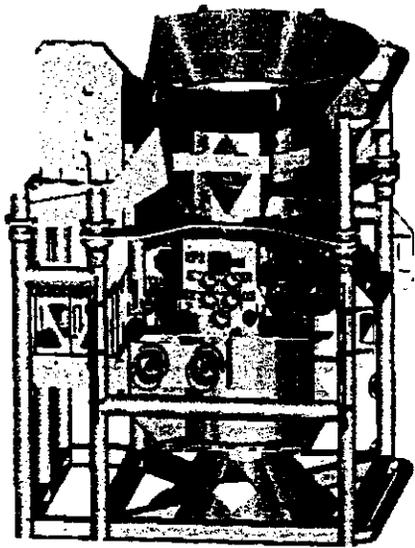
Figure 2: Horizontal tree

X

Tree Cap

Tree Frame

Tree Master
Valve Block

Tree Connector

Tubing
Spool

Tubing
Hanger

Wellhead
Connector

Wellhead

Drilling
Template

Production
Guide Base
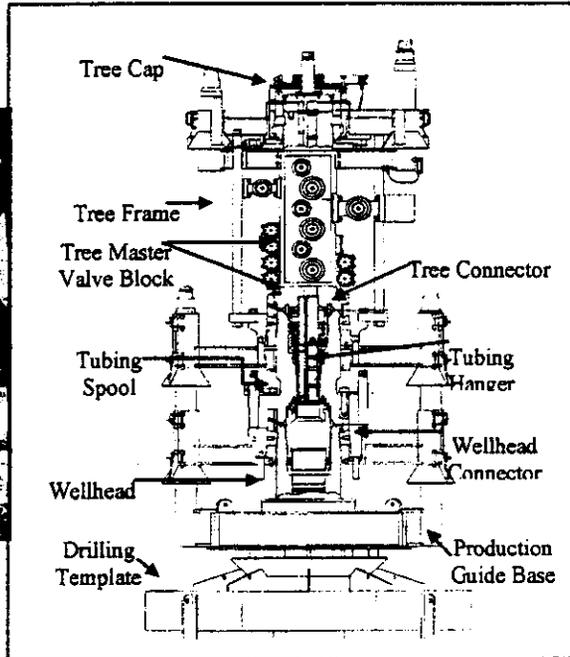
Figure 3: Vertical Tree

4.2. Flowline Jumpers

Short sections of piping are used to connect the production tree with either the manifold or direct lowline tieback system. The jumper can consist of single piping or a more complex bundled arrangement, as shown in Figure 4. Again corrosion protection can be difficult given the need to provide thermal insulation. As a rule the jumper piping is not isolated from the production tree. Material selection is normally based on production conditions.
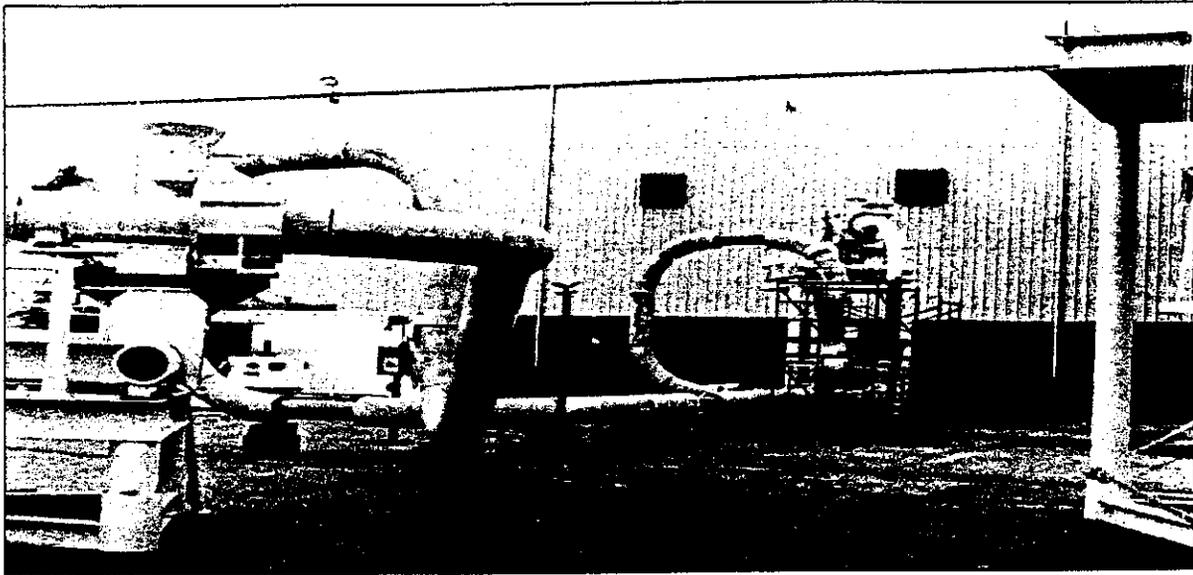
Figure 4: Insulated jumper pipeline

4.3. Umbilical Termination Assembly

Umbilical Termination Assembly (UTA) connects the subsea equipment to surface facilities or other subsea equipment. The UTA mechanical, electrical, and hydraulic connectors are made out of dissimilar materials with different corrosion characteristics. The chemical compatibility of the inhibitor lines and chemical lines along with electrical supply lines should also be considered in the design.

4.3. Manifold/Templates

When commingling of the production fluid is required, either a manifold or template is used. Cluster manifolds are gaining wider use because of the large extent of most deepwater reservoirs. Typical template and cluster manifold designs are shown in Figures 5 and 6. Large subsea structures such as manifolds may have complicated geometry and hard to access locations, therefore distribution of CP is a critical design parameter. Marine coatings and cathodic protection are used to control marine corrosion, whereas material selection for valve and piping components will normally be dictated by the production conditions. The use of thermal insulation can be a problem with regard to cathodic shielding. It should also be noted that manifolds are partially buried structures, therefore interaction between the manifold material and the seabed should be considered in the design.
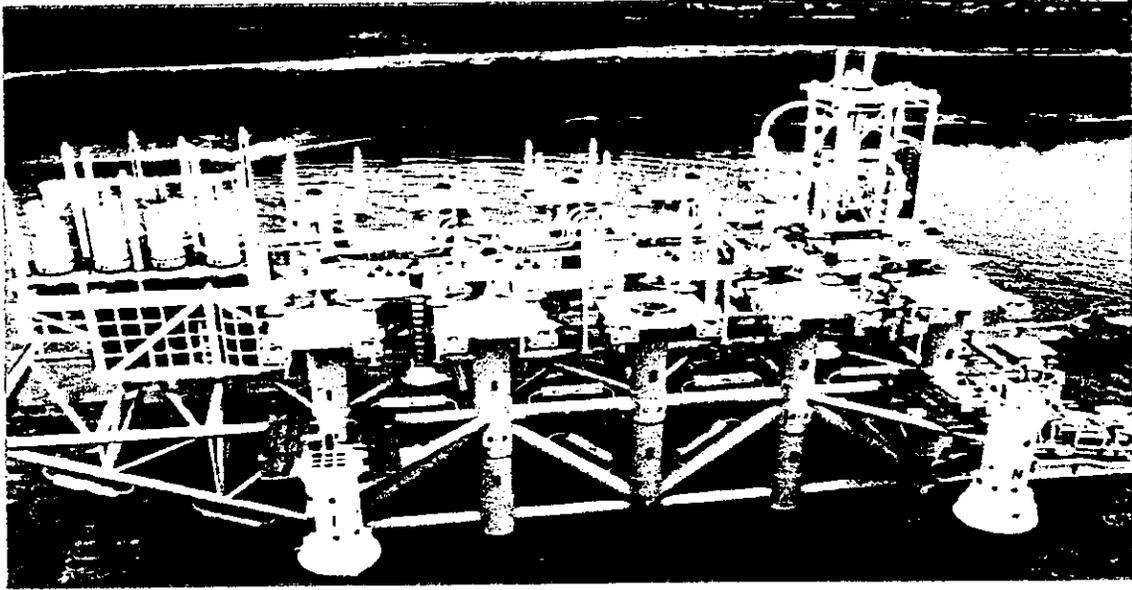
Figure 5: Template Manifold
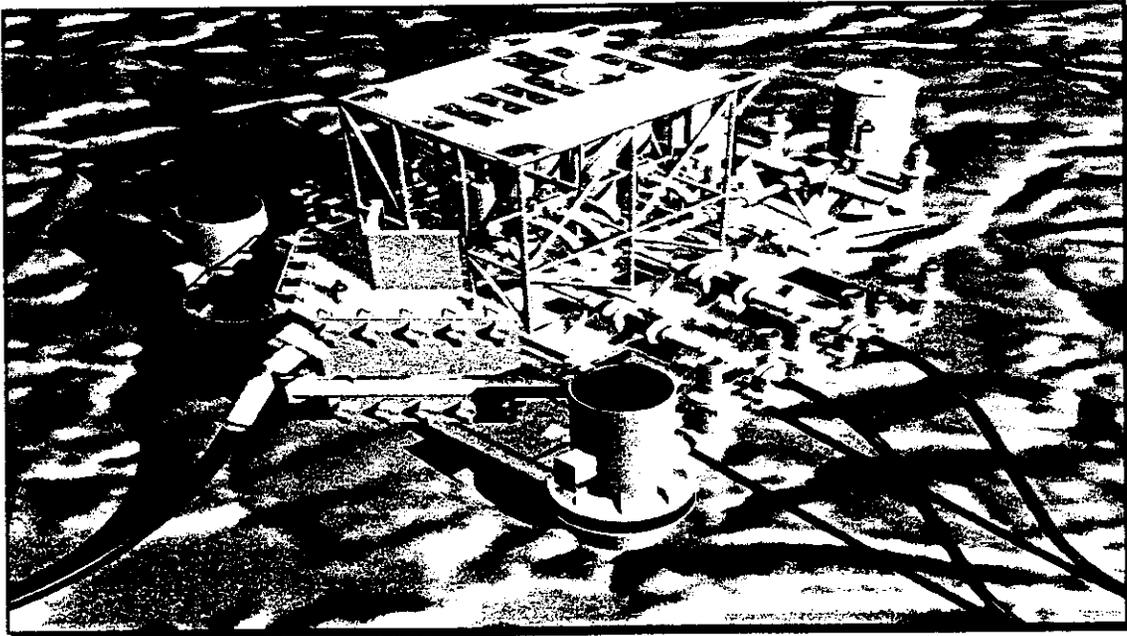
Figure 6: Cluster Manifold

4.4. Subsea Separation

Subsea separation technology is currently being developed to facilitate stand-alone field development to improve fluid flow in long tieback flowlines and to remove excess water from the wellstream prior to arrival at the host production facility. A typical subsea separation unit is shown in Figure 7, which have numerous critical small components, such as valves, connectors, and tubing. These small components are critical in the operation of the units, yet the corrosion protection of these components can be easily achieved with proper CP methods. These issues need to be addressed at the early in the field development process.

Material selections for the separator equipment and water re-injection pumping unit will be dictated by the production fluids, whereas marine corrosion protection is provided in the form of coatings and cathodic protection. Subsea separation units may require high electrical power, which may disturb the electrical fields and alter the conventional corrosion characteristics of the equipment surface.
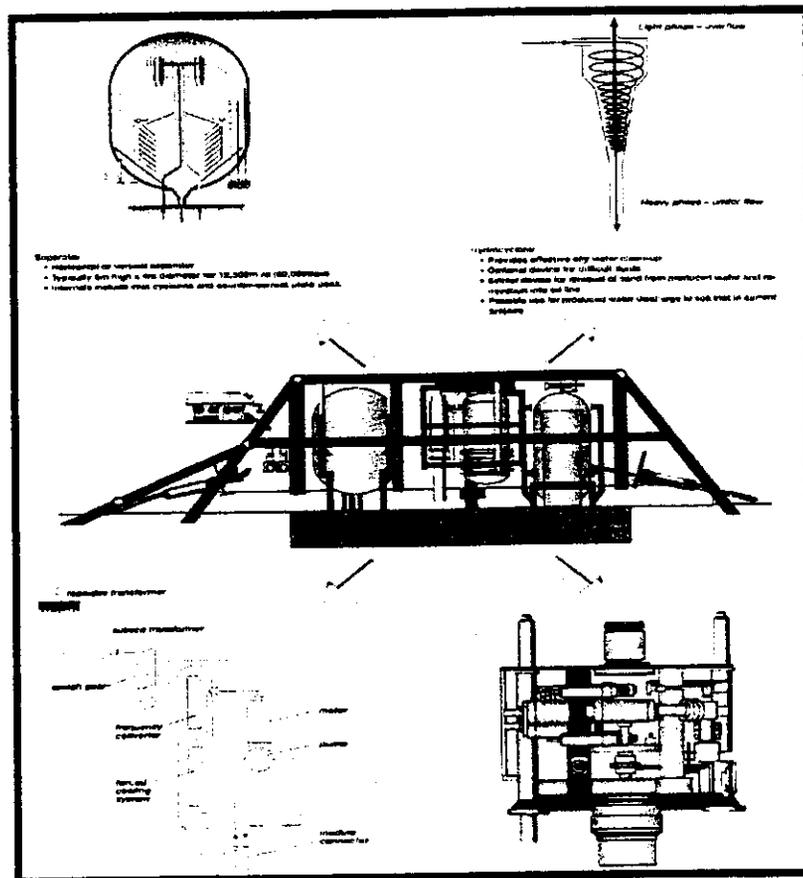
Figure 7: Subsea Separation System

4.5. Subsea Booster Pumping

Subsea booster pumping is used in combination with subsea separation or as a stand-alone unit. Subsea booster pumps are being developed to enhance deepwater reservoir performance as well as enable extended tieback of multiphase fluids. A typical subsea booster pump field layout is shown in Figure 8, with the booster pump assembly itself shown in Figure 9. Corrosion protection of the booster pump assembly will rely on corrosion coating and cathodic protection.
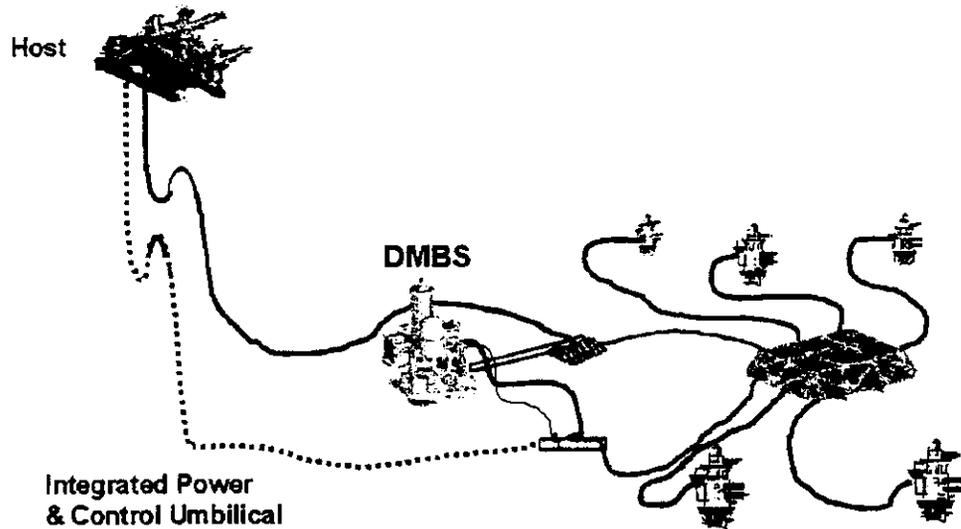
Figure 8: Subsea Multiphase Booster System Layout
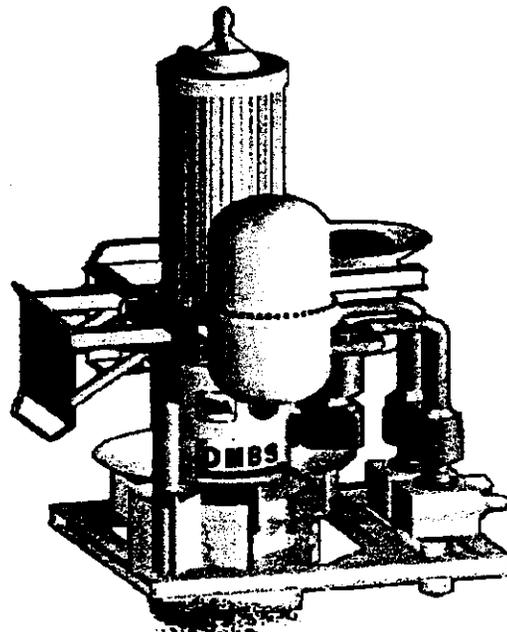
Figure 9: Booster pump assembly

5. Maintenance, Modification, Retrofit and Abandonment

Maintenance, modification, retrofit, and abandonment issues play a critical role in technical and economic feasibility of the deepwater subsea equipment applications. The lifetime cost of a deepwater system significantly depends on the maintenance cost. A maintenance free design may have a very high initial cost, which can make the project economically unfeasible. On the other hand, operation costs of a high maintenance system may also make the system economically unfeasible. In addressing corrosion protection issues, a balance between the capital and operation expense needs to be established. Inspection and maintenance of the selected CP method needs to be established. Retrofit of the CP systems may be required for coating repair, anode retrofit, and removal of debris and mud.

Modification of the subsea equipment may be required when the production and operation requirements change. A system can be designed for significant modifications such as additional tie-in systems with different CP requirements and removal/addition of modules and piping. The system should not disintegrate at the end of service life. Proper abandonment procedures may need to be demonstrated to satisfy regulatory requirements.

6. Corrosion Protection Review

Carbon and low alloy steels are the most cost-effective materials for subsea equipment and systems. However, these materials require corrosion protection for reliable and safe long-term operation. More corrosion resistant materials may be cost effective for small components, particularly, where a small amount of corrosion has a significant effect on the system function. Based on lifecycle cost, selection of material and accompanying corrosion protection methods can make a significant difference in feasibility of subsea equipment and systems. Hence, design of subsea systems with respect to corrosion should consider operational, technical, and life cycle cost as a function of the field lifetime of the system(s).

Subsea equipment and facilities are complicated systems with many functional parts. Different types of materials (low alloy steels, stainless steel, CRAs, polymers, composites, ceramics, etc.) and corrosion protection techniques may be used for different parts of the subsea system. Numerous methods are available for corrosion protection of the deepwater subsea systems. An optimal corrosion protection method should consider selection of material and associated corrosion protection technique simultaneously for the whole subsea system.

Application of anti-corrosion coatings is the most common method to reduce the corrosion rates. A wide range of coating materials and application methods have been developed for such use:

- Glass fiber reinforced asphalt enamel + concrete weight coating (pipelines)
- Polypropylene or polyethylene coating (pipelines)
- Polychloroprene (neoprene) rubber (risers & pipelines & structures in splash zone)
- Fusion bonded epoxy (FBE) (critical components)
- Zinc based primer + epoxy based intermediate coating + top coat (structures)
- Thermal sprayed aluminum coating (risers & closed compartments)

Corrosion protection coatings are susceptible to water absorption and general degradation of the coatings. Cathodic protection (CP), in combination with surface coating, is commonly used to protect external surfaces of subsea equipment. Cathodic protection can bring the steel surface into a passive region where the corrosion rate is significantly reduced. Figure 10 illustrates the sacrificial anode and impressed current corrosion protection methods applied for protecting subsea structures.

Sacrificial anode alloys, such as Zinc or Aluminum, are installed at the critical locations. The size and selection of the anodes depends on the following factors:

- Design life of the system to be protected
- Type and quality of the applied coating
- Structure surface area
- Coating coverage
- Selected materials
- Anode material types
- Interaction with connected structures
- Water and steel temperature
- Oxygen content in the water
- Microbiological activity
- Resistivity of the environment
- Drilling mud, cuttings and seabed coverage of components

In order to secure corrosion protection to all components, all interfaces must be evaluated and electrical continuity straps must be installed where required.

The most usual anode geometries applied today are:

- Stand-off/slender anodes (structures)
- Flush mounted anodes (structures)
- Bracelet anodes (pipelines and tubular structure beams)

Different design standards are developed specifically for different areas in the world, and are generally based on field measurements, long term experience, and laboratory experiments. Computer models can be used to evaluate corrosion protection of complicated structures/parts, interface problems, and when uneven anode distribution is foreseen.

7. Corrosion Monitoring and Inspection

7.1. External Corrosion Monitoring

External corrosion monitoring systems for subsea equipment are designed to monitor the efficiency of the cathodic protection system. The types of monitoring equipment and monitoring frequency are dependent on the criticality, corrositivity, and lifetime of the structure/system.

Permanently mounted sensors are used for cathodic protection monitoring of critical and inaccessible components. These sensors can measure electrochemical potential of the equipment surface, current output from selected anodes, or current density depending on the application. Sensor measurements are calibrated against high purity zinc reference electrodes or Ag/AgCl reference electrodes.

The external corrosion control system consists of a number of sensors placed at critical locations of the subsea facility. The status of the subsea facilities can be monitored online by a continuous corrosion monitoring computer system. Alternatively, sensors can be monitored at regular intervals. Statistical techniques are used to process the acquired data for both monitoring approaches.

7.2. External Corrosion Inspection

External corrosion inspection is essential to establish the status of the corrosion protection. Inspection can be used in addition to monitoring, as a check of the monitoring system or as the only method to check the efficiency of the corrosion protection system.

The methods available for inspection are as follows:

- Stabbing of structures and anodes with a reference cell based equipment. Use of ROV to check protection potential and anode activity.
- No contact measurement with reference cells. ROV can be used if sufficient electrical grounding to the structure to be inspected can be achieved.
- Stabbing of structures and anodes by use of two or more reference cell based equipment. ROV can be used to check protection potential current density requirements of the structure and anode current output.
- Special clamps to "anode feet". ROV can be used to measure anode current
- Visual inspection of structure. To check coating quality and metal surface
- Visual inspection of anodes. To check anode performance and remaining weight

The stabbing equipment requires metal to metal contact to achieve measurements. This will in worst case damage corrosion coating. In order to avoid this problem, inspection points should be included on the structures in the design/construction phase. This can be achieved by preparing small surface area (approx. 100 cm2) with only primer or even bare metal. The surface area of these inspection points must be included in the CP design according to the selected condition (primer coating or bare steel). All inspection points must be readable marked.

It is recommended to prepare inspection plans on a 3 to 5 year basis. The inspection planning should include element as equipment criticality and utilize inspection data, monitoring data and historical data to be able to perform minimum inspection and secure integrity of the corrosion protection system.

7.3. Internal Corrosion Monitoring

The objective of internal corrosion monitoring system is to verify that the real internal corrosion rates are within the design criteria and predicted rates. Type of monitoring equipment and monitoring frequency is dependent on the criticality, corrositivity, and lifetime of the structure/system.

The location of the corrosion monitoring unit is of vital importance to ensure that the collected data reflects the actual corrosion conditions of the subsea system. During the design phase, the predicted corrosion profile should be analyzed and used as basis for the corrosion monitoring equipment evaluations.

Accurate internal corrosion monitoring of the subsea equipment allows for selection of different material systems and to reduce the corrosion allowance requirements. For example, carbon steel in combination with inhibitor treatment can be selected as an alternative to Corrosion Resistant Alloys(CRA). Internal corrosion monitoring of subsea equipment and pipelines is often used as basis for:

- Optimization of inhibitor injection programs,
- Optimization of process conditions based on correlation between monitored corrosion rates and process conditions,
- Possibility to make corrective actions to reduce corrosion rates and possibly extending operating life of the components.
- Indication of when certain parts of the system have to be replaced.

Modern corrosion monitoring systems offer online communication with the sensors and fast processing of the acquired data, which facilitates optimization of the process conditions and inhibitor injection programs. Corrosion monitoring systems use the following communication techniques:

- Cable based communication/power from subsea corrosion monitoring system to topside,
- Hydroacoustic data communication with Subsea Control Systems (battery operated subsea unit).

Available subsea corrosion monitoring systems are:

- Electrical Resistance(ER) probes (Figure 11a)
- High Sensitivity ER probes (Figure 11b)
- Field Signature Method (Figure 12)
- Ultrasonic Monitoring Systems

For day-to-day operations and use of the corrosion monitoring systems a PC based program is used for evaluation of relevant corrosion monitoring data giving:

- Corrosion trend analysis,
- Accumulated metal loss,
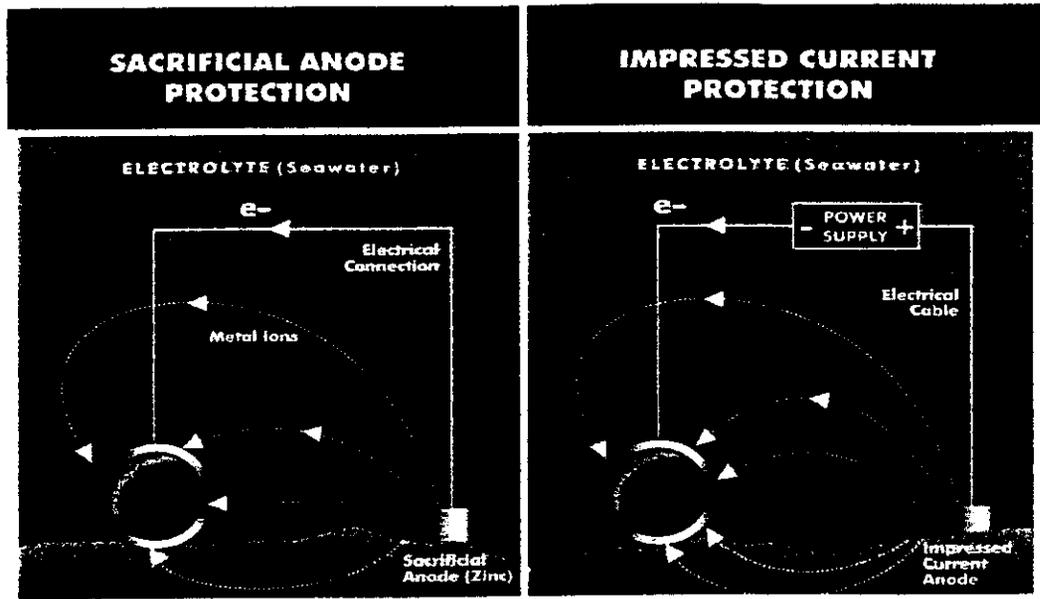
Figure 11: Corrosion protection with anodes.
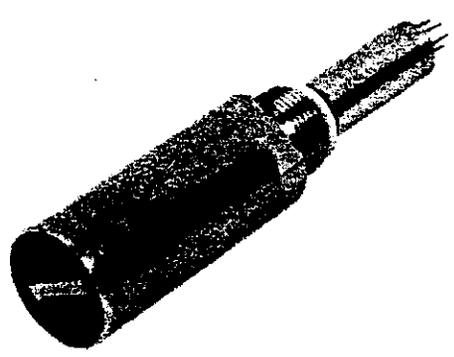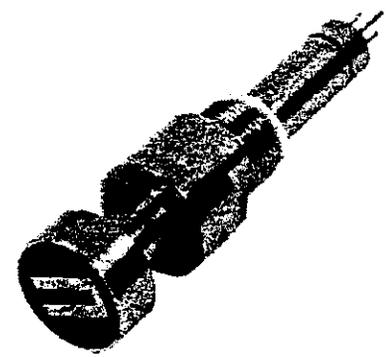
(a) ER probe

(b) High Sensitivity ER probe

Figure 12: Electrical Resistance Probes to Monitor Material Loss from Erosion

8. Closure

The corrosion issues of deepwater subsea systems are identified as follows:

1) A comprehensive materials database is needed. This database should cover material classification as a function of deepwater corrosion mechanisms, material performance limitations, and advanced materials along with the galvanic interaction of those materials.

2) Deepwater subsea equipment and facilities are complicated systems consisting of numerous materials operating under wide range of conditions. The material compatibility of multi-phase systems is a design consideration.

3) In order to justify the system reliability, a balance between system risk and system cost of needs to be established. Initial and lifetime costs of deepwater systems may define the feasibility of many subsea applications.

4) The following issues may be considered in the deepwater corrosion design philosophy:

    a) Design for much longer than field life. Overdesign to reduce risk of failure when economically feasible.

    b) Establish methods to quantify cost versus risk in order to assess system reliability. Develop risk based material selection criteria.

    c) Establish project economic drivers, balance initial versus lifetime cost

    d) Reduce or eliminate hotspots on the complicated systems. Pay attention to low cost component details, such as bolts, fasteners, and electrical connectors.

    e) Provide integrated total system design. Simplify the system design.

    f) Develop design guidelines for deepwater corrosion protection system selection

    g) Capture information on stray currents that may be control signals coming through the riser or intervention work-over lines.

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CORROSION CONTROL FOR SHIP STRUCTURES

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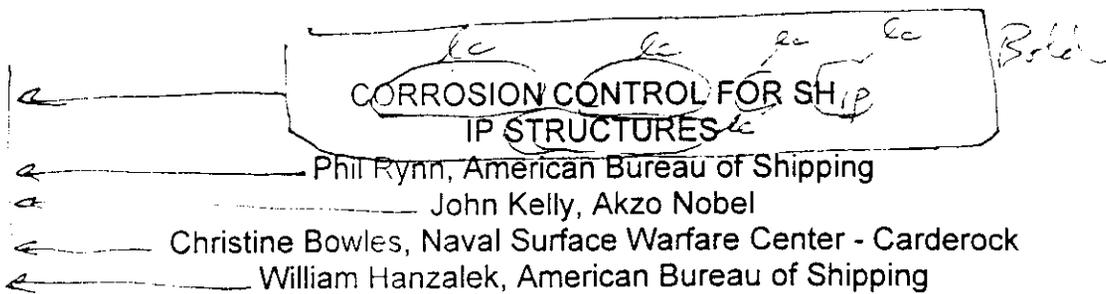
ABSTRACT

This report summarizes the current status of corrosion prevention approaches for various ship types and ship systems, and identifies good practice approaches for corrosion prevention. Recommendations for future work are also presented.

CORROSION PREVENTION PHILOSOPHY

The technology of corrosion prevention methods is continually improving, and thus affords users with ever increasing choices of coatings and cathodic protection systems applicable to ships. Combinations exist that can reasonably assure freedom from a disabling corrosion for the life of the vessel, but of course, the superior systems carry a greater expense. The ship owner must identify needed performance of the vessel in terms of service use and service life. In general the basic approaches as to the level of application of corrosion prevention technology can be summarized as follows:

- No Protection (wastage allowance)
- Protective Coatings
- Cathodic Protection of Bare Steel
- Cathodic Protection of Coated Steel
- Corrosion Resistant Metallic or Plastic

Consideration of a specific corrosion prevention technology or system (CPS) to be used for a particular ship system, must include standard engineering evaluation that takes into account not only the anticipated resistance to the environment and the anticipated duration of the CPS, but also the ease and expense of application, and the ease and expense to repair damaged coatings or depleted anodes. In certain cases and due to economic reasons, repair may involve a different coating or supplementary technology.

- 1 -

The application of the corrosion prevention technology as typically carried out today is addressed herein as to the various important ship types and ship systems.

COATING APPLICATION FACTORS

Probably the most important factor in the application of a coating is the preparation of the surface. The steel surface must be clean, dry and free from water soluble salts and oily residues that can lead to poor adhesion and premature rusting. In addition the steel surface must exhibit a 1 to 2 mil (thousandths of an inch) profile for the coating to properly adhere. The profile is the distance from the peak to the valley of the surface pattern resultant from abrasive blast cleaning. In general, most coating manufacturers specify a near-white blast, or for special coatings a white-metal blast (see Table One).

Other application factors related to the coating are also recommended by the manufacturer and normally include a metal, air and coating temperature range, proper ventilation, freedom from contamination, and correct spraying procedures including the specified dry film thickness. Controlling the parameters requires a certain expertise, especially for the high performance coatings intended to protect the inside of tanks. Most shipyards contract out this type of coating application to specialist companies, and do the exterior and the less critical interior coating applications themselves.

VLCC CARGO SYSTEMS

This section covers cargo tanks, that is tanks which predominately but not always are used for the carriage of cargo. These tanks may be used to carry storm ballast, and so will experience some seawater service, although not routinely. They are however exposed to a water environment at the bottom due to water settling from the crude cargo.

Cargo tanks may or may not be coated at the option and opinion of the owner as to the severity of the corrosive attack during service. In general the severity of the attack is thought to be somewhat less than that which existed about 15 years ago. International regulations effective from the mid 1980's have eliminated cargo/ballast tanks and have mandated that certain systems intended to reduce the likelihood of pollution be installed. These are gas inerting and crude oil washing.

Crude oil washing has the advantage of minimizing the amount of seawater (previous to COW, tanks were washed with seawater, or worse yet with hot

seawater) that the tank experiences, thus minimizing corrosion which is enhanced by seawater. However, COW also removes protective waxy deposits, may damage coatings, and can actually scour steel due to high pressures. In addition, tank surfaces missed by the COW may behave cathodically to cleaned surfaces and thus accelerate corrosion on a local scale.

Gas inerting tends to reduce corrosion of the underdeck structure by lowering the atmospheric oxygen content, which is needed for corrosion to proceed. However, the total effect of the inerted gas is a function of the source of the gas. The type of gas inerting commonly used for VLCC's is flue-gas based, and typically contains high levels of sulfur dioxide and similar sulfur based gases which by nature are corrosive to steel. On the other hand, independently generated gases typically contain low levels of these sulfur based gases and are less harmful, but these systems are more likely used on vessels such as product carriers or chemical carriers.

At neither the tank bottom, lower horizontal surfaces, or underdeck structure is the severity of corrosion less than that for the non-horizontal structure, eg. the side shell, webs and longitudinal bulkheads, where corrosion is typically quite low.

Where coatings are opted to be used they are normally confined to the bottom and about six feet up the side shell and to the underdeck and about six feet down the side shell. Coal tar epoxy is generally used, although inorganic zinc coatings may be used for the bottom where sweet crude is carried, but not for the underdeck due to attack by surfur-based, flue-gas inert gas systems. In way of the suctions and at other sites where erosion is a concern, the epoxy is reinforced with glassflake.[1]

Pit guard anodes are sometimes fitted to the bottom in bays where the water wedge is anticipated. Aluminum anodes which self-clean of crude oil are preferred to zinc anodes, however, the use of aluminum anodes is limited by regulations which restrict the height above the tank bottom due to the risk of explosion if the anode falls and sparks on impact. In general the use of supplementary anodes tends to increase the useful life of the coating (see Table Two).

Aluminum, in the form of a hot-dipped aluminized layer, has also been used to mitigate corrosion on the external surfaces of deck steam piping. The piping is intermittently used to transport the steam leading to a cyclic temperature service where organic coatings are not satisfactory. As the piping is located in hazardous areas, safety issues must be considered, specifically the hazards resultant from sparking. It is recommended that further research be carried out to evaluate sparking hazards associated with aluminized surfaces.

Recent experience with uncoated cargo tanks has shown an accelerated in-line corrosion attack, and has initiated studies regarding the type of steel (TMCP) used in the construction as being contributory to this failure mode. While it is recognized that the special steel processing inherent to TMCP steel introduces some 'texture' to the steel, no investigation to date has identified a relationship to a higher level of corrosion. In addition, microbiological corrosion (MIC) has been suggested as the relevant mechanism for other 'unusual' types of pitting corrosion found in cargo tanks. Again, published investigations are not conclusive on this point. It is suggested that further research be carried out that addresses accelerated corrosion specific to TMCP steel, and addresses accelerated corrosion specific to MIC attack and ways to economically mitigate.

CHEMICAL CARRIER CARGO SYSTEMS

This section covers cargo tanks, that is tanks which predominately but not always are used for the carriage of cargo. These tanks may be used to carry storm ballast, and so will experience some seawater service, although not routinely. However, they are routinely seawater washed between carriage of different cargoes.

The type of refined product carried together with economic considerations will dictate the type of corrosion resistance scheme used. The principal concerns are resistance to the refined media, and contamination of the cargo in which case coatings that behave in a sacrificial manner cannot be used. For example, inorganic zinc coatings cannot be used with acidic cargoes due to contamination by zinc salts as well as break down of the coating (in fact IOZ has low resistance to strong alkalis as well and is not recommended for service outside the pH range of 5 to 10). However, solvent-based inorganic zinc coatings that have been topcoated and thus sealed by a non-zinc ethyl silicate coating have successful product carrier service.[2] As an analogous limitation, coal tar epoxy coatings cannot be used with solvents.[3] These limitations of the coating have restricted the owner in the carriage of cargoes. The basic properties of three type of epoxy are shown at Table Three.

To increase the flexibility in carriage of varying cargoes, many owners have chosen the use of a corrosion resistant metallic for the surfaces of the tank that are exposed to the cargo. Corrosion resistant metallics are inherently safer than coatings (especially important for cargoes that can attack steel such as acid) which may be penetrated thus exposing the underlying steel. But corrosion resistant metallics are more expensive than coatings.

The most common is a: alloy of austenitic stainless steel, usually a low-carbon type to avoid corrosion at the HAZ. The majority of applications use clad steel, where a relatively thin layer ($\approx$ 2mm) of stainless steel is bonded to a much thicker (12-15mm) substrate of structural steel. The original material procurement costs are lower than solid stainless steel, but fabrication is more difficult in that many welds are two-part: a ferritic weld metal to join the structural steel substrate, and an austenitic weld metal to join the stainless cladding. Where strong chemicals such as acids, are carried, the thickness of the clad layer may be increased to give protection against mechanical damage which could lead to rapid penetration of the steel substrate. A more conservative and expensive approach here calls for solid stainless steel, typically 316L or 317L. Duplex stainless steel has also been used and due to the higher strength than that of austenitic stainless steel can offer design enhancements.

Harder coatings are also used and include phenolic epoxies. These, however, are subject to absorbtion of the cargo and the threat of contamination of the cargo next carried. Recently high-density, cross-linked organo/silicon-oxide thermoset resins have shown excellent resistance to many cargoes, including acids.[4] These coatings have been applied on a limited basis with good success, and have demonstrated integrity over buckled steel structure.

BULK CARRIERS

Large deep holds of bulk carriers where the cargo is non-abrasive (like grain) are normally coated with several coats of coal tar epoxy or a modified tar free anti-corrosion epoxy coating. Where the cargo is abrasive, such as, coal, sulfur, phosphate rock, iron ore, etc., an abrasion resistant pure epoxy applied in 2 or 3 coats should be used. The coating will require frequent repair, which must be carried out, since these cargoes when wetted frequently produce an acidic element that can readily attack the steel hold. In the past, the holds of bulk carriers carrying abrasive cargoes were left uncoated, however, severe metal wastage and resulting dangerously weakened structure has caused this approach to be rethought.

The requirements for dry cargo spaces in smaller vessels are not considered stringent. A lower level of surface preparation, SSPC SP-6 (commercial blast), is considered adequate. The coating is normally two-part: a light colored enamel over a corrosion resistant primer.[5]

BALLAST SYSTEMS

Segregated ballast tanks are normally fully coated and often the corrosion prevention system is supplemented with zinc anodes to delay coating breakdown at holidays and at sharp edges and corners. Epoxy and coal tar epoxy coatings are preferred, although inorganic zinc coatings have been used and with backup anodes give acceptable performance.[6]

The implementation of a full, hard coating system is required by the International Maritime Organization for bulk carriers and for oil tankers built after 1996. A hard coating used for newbuildings is defined as one which chemically converts during the curing process. A hard coating used for the repair of damaged coating on existing vessels is defined as above and in addition as a non-converting , air-drying coating.[7] Thus for bulk carriers and for oil tankers, the sole use of a sacrificial cathodic protection system or the sole use of soft coatings or the sole use of uncoated steel is not permitted.

The situation is slightly different for other types of vessels in that soft coatings are permitted, but where so the tank is subject to annual survey.[8] For bulk carriers and oil tankers, the use of soft coatings is allowed as a temporary measure for maintenance purposes however, these tanks must also be surveyed on an annual basis during which the soft coating must be completely removed to ensure a satisfactory inspection.[9,10] Soft coatings are candidates for maintenance purposes since the level of surface preparation (SSPC SP2, hand tool cleaning) is much reduced from that needed for a hard coating.[11] A soft coating is defined as one that wears off at a low mechanical impact, by walking on, or even only when touched by hand. These coatings are typically grease based, petroleum based, or vegetable oil based.

In the past, zinc anode or aluminum anode (magnesium anodes are never used due to the generation of hydrogen gas with attendant risk of explosion) sacrificial cathodic protection has been used in seawater ballast tanks, but does not afford total protection. Corrosion can occur during the period of anode polarization and in the humid atmosphere after deballasting, particularly at a bulkhead of a heated cargo.[12]

Provided the current density can be increased to shorten the polarization period and then reduced to steady-state maintenance levels, the protection efficiency for mild structural steel is shown to be greater than 90 percent.[13] Frequent modification of current densities is practically accomplished by means of impressed current systems. These, however, are never used inside tanks of commercial vessels, although the US Navy has studied and modeled impressed current systems as a replacement for zinc anode sacrificial systems.[14]

EXTERIOR HULL

The corrosion prevention system to protect the steel hull is usually two-part consisting of barrier coatings and a cathodic protection system. The coating it self may be multifunctional in that at least the outer layer must resist fouling by marine organisms.

Antifouling coatings are of several types but basically minimize biofouling by the slow release (non-polishing or self-polishing) of metallics or compounds that are toxic to the offending marine life.[15] Copper-based metallics (cuprous oxide) have traditionally been used but have fallen from favor due to variable performance, and the potential for becoming cathodic to the underlying steel.[16,17] Tin-based (organo-tin) antifoulant coatings, such as tributyl tin oxide or tributyl tin fluoride, are very effective in preventing fouling by marine organisms, but have been restricted by environmental concerns and resulting legislation.[18,19]

Current effort is focusing on the application of silicone type top coatings with non-adherent surfaces which prevent organism attachment, and is focusing on the use of naturally occurring antifoulants, eg biochemicals found in coral and sponges that are considered environmentally acceptable.[20,21]

Commercial vessels generally use epoxy coatings as the primary protection against underwater corrosion.[22] These coatings are supplemented by zinc sacrificial anodes arranged on the hull to account for holidays in the applied coating, local damage breakdown to the coating, protection of seawater inlets and other hull penetrations, and protection of uncoated components such as bronze propellers.

Military vessels also employ a primary system of barrier coatings and a secondary cathodic protection system, but the CPS used is impressed current rather than sacrificial anodes.[23] The applied current is regulated by continual monitoring of the hull potential to achieve –850 mV versus Ag/AgCl reference cell. With larger vessels, the impressed current system is divided into multiple zones that are independently monitored and controlled. This approach takes into consideration hull geometry and wetted surface area and can provide more uniform polarization of the hull.

A combination system of coal tar epoxy coating, zinc anodes and an impressed current cathodic protection system has been shown to be 100 percent effective and very efficient in preventing hull corrosion.[24] The impressed current system incorporated automatic potential control to be responsive to operating factors which influenced the current density requirements such as vessel speed, water turbulance, water oxygen content, water chloride content (electrical resistivity), presence of hydrogen sulfide, etc. For these vessels the current output of the

combination system was reduced to 1.5 to 2 amps from about 100 amps for the zinc anodes without supplemental impressed current.

The effect of the velocity of flowing seawater is a factor in the maintenance of calcareous deposits as shown by polarization and subsequent repolarization at velocities about 0.1m/sec and higher.[25] This calls into question the reliance on sacrificial anodes and formation of protective calcareous deposits to reduce the maintenance current densities as a long-term effective solution for higher velocity seawater systems, eg those for external hull protection.[26]

The combination of barrier coatings and cathodic protection can be effective over the life of the vessel. Current improvements focus on minimizing the costs associated with the cathodic protection system, eg reducing sacrificial anode replacement and reducing impressed current system energy.

For the boottop (the intermittantly wetted region between the light load line and the deep load line) and up to the gunwale or rail, urethane topcoats are used over epoxy mid-coats and inorganic zinc base-coats.[27]

TOPSIDES AND SUPERSTRUCTURE

The topsides and superstructure, including the exposed strength deck or weather deck, are considered to be for the most part less critical applications than most of those already addressed. The weather deck should be prepared to near-white (SSPC SP10), base coated with inorganic zinc and finish coated with chlorinated rubber, vinyl, epoxy, or urethane. Non-skid additives are to be considered.[28]

The topsides and superstructure are shown to use a wide range of coatings from pure epoxies to urethanes to alkyds. All are generally topcoated over an inorganic zinc, or other anti-corrosion base coat of suitable compatibility. Anti-stain and low solar absorption cosmetic finishes are used.

DRY SPACES

Dry spaces are minimally coated if at all. Inaccessible and sealed voids may or may not be coated, but should be coated. Accessible voids and cofferdams may be coated by means of a zinc rich coating or may be coated with coal tar epoxy or modified epoxy.

DESIGN ISSUES

Today, many ship struc...ures are designed with consideration given to corrosion prevention. Newer double-hull tankers designs take into account human access for inspection and maintenance as part of the overall corrosion prevention approach.[29] Hot-rolled bulb flats and angles are ordered for construction to minimize water trappage and to reduce sharp corners and edges. Weldment surface acceptance criteria that are more conservative than welding workmanship standards are specified to increase the likelihood for good coating adherence. Similarly, at surfaces, edges and corners of welded shapes and internals are ground to a suitable ($\approx$2mm) radius to promote good coating adherence and long-life adherence. It is recommended that designers work with corrosion specialists to identify new areas where appropriate changes to design and proper application of product types will lead to good coating adherence, service inspection, and ultimately good corrosion prevention over the life of the vessel.

NOVEL SOLUTIONS

In addition to the conventional use of organic and inorganic coatings, and the use of CPS to protect ship structure, new solutions involving thermal spray technology have been tried with good success. Thermal spraying is a high temperature application method whereby steel structure can be coated with either barrier coatings or sacrificial coatings to protect against corrosion. This technology has been used principally by the military, and has very little application by commercial shipping. Aluminum, zinc-aluminum, and zinc coatings have been used.[30]

Thermal spraying of plastic coatings offers a promising means of protecting structure and equipment from the effects of corrosion in marine environments. Unlike traditional multi-coat painting processes, polymer spraying is a one-coat process that acts as both the primer and the sealer, with no additional cure times. Thermal spraying is ideally suited for large structures. Thermoplastic coatings can be repaired by simply re-melting or applying additional material to the desired location, and are ideally suited for in-field repair and recoating operations. Polyethylene. polypropylene, grafted polyethylene copolymers, fluoropolymers, polyesters. nylons, and some thermosetting resins have been sprayed to produce coatings.[31,32] In addition, reports have shown that functionalized polyethylene polymers such as EMAA and ethylene acrylic acid (EAA) can be applied in high humidity as well as in temperatures below freezing.[33]

Thermal spray technology is beneficial as regards compliance with increasingly restrictive environmental regulations to reduce or eliminate volatile organic compounds (VOCs), hazardous air pollutants (HAPs), and hazardous materials,

particularly for special: coatings, such as erosion-resistant, ultraviolet (UV) radiation-resistant, and fire-resistant coatings. Significant cost savings are realized when the lifecycle costs of thermal spray plastic coatings are considered relative to solvent-based coatings. Thermal spray coatings require no curing or baking, which means that coated parts can be returned to service immediately after coating application. This minimizes system downtime and eliminates the need to shroud the part to be coated and condition the environment within the shroud to maintain optimum conditions (temperature and humidity) during curing. Field repairability and increased performance also contribute to the lifecycle cost savings of using thermal spray plastic coatings. It is recommended that research continue for the development of thermal spray coatings, particularly thermal spray plastic coatings.

CONCLUSIONS FOR GOOD CORROSION PREVENTION PRACTICE

To achieve good resultants with corrosion prevention systems the following should be considered.

A. The integrity of tank coatings depends on:
  i) Doing it right the first time by:
    a Proper surface preparation
    b) Grinding free edges to remove sharp corners
    c) Stripe coat welds and free edges
    d) Use proper inspection and quality control, and maintain dialog with shipyard during construction and coating application
  ii) Employ continuous service maintenance
  iii) Use secondary CPS, anodes

B. Expand use of composite materials.

C. Promote awareness of MIC attack in water ballast tanks and in cargo tanks.

D. Study all environmental factors before applying coatings to novel of unusual service.

RECOMMENDATIONS FOR FUTURE WORK

The following areas have been identified where further research and work is needed to develop knowledge or to resolve unanswered questions.

1. Evaluate and quantify sparking hazard risk of aluminum containing coatings.

2. Determine whether TMCP steel is susceptible to accelerated corrosion in tanker structure.

3. Investigate factors leading to MIC attack and develop an economic means to mitigate.

4. Develop coating friendly designs and service inspection friendly designs for ship structure.

5. Explore the expanded use of thermal spray coatings for commercial vessels, and the suitability thermal spray plastic coatings for all vessels.

6. Improve corrosion monitoring systems, sensors and devices for evaluation of protection systems during service.

7. Develop cost effective methods for tank coating inspection, repair and maintenance for existing vessels.

REFERENCES

[1] *Corrosion Control on Tankers,* W.H. Bray, 28th Annual Marine and Offshore Coating Conference, May 1988.

[2] *Marine and Offshore Corrosion Control,* Munger, C.G., Materials Performance, September 1993.

[3] *Investigation of Internal Corrosion and Corrosion- Control Alternatives in Commercial Tankships,* Ship Structure Committee, SSC-312, 1981.

[4] Advanced Polymer Sciences literature, 1997.

[5] *Painting of Vessel for Salt Water Service,* Bloodgood, D.T., Steel Structures Painting Manual, Vol. 1, 3rd Edition, 1994.

[6] *Tank Coating Guide for Ballast Tanks of All Vessels and Cargo Tanks of Petroleum Tankers,* SNAME Technical & Research Bulletin No, 4-23, The Society of Naval Architects and Marine Engineers, 1991.

[7] *Guidelines for the Selection, Application and Maintenance of Corrosion Prevention Systems of Dedicated Seawater Ballast Tanks,* Resolution A.798(19), International Maritime Organization, 23 November 1995.

[8] SOLAS/CONF.4/25, Safety of Life at Sea

[9] *Survey Guidelines for Tanks in Which Soft Coatings Have Been Applied,* Recommendation No. 44, International Association of Classification Societies, 1996.

[10] SOLAS/CONF.4/25, Safety of Life at Sea

[11] *Guidance Notes on the Application and Maintenance of Marine Coatings,* American Bureau of Shipping, 1998.

[12] *Factors Contributing to Corrosion,* Tanker Structure Cooperative Forum, Project 102, 1984.

[13] *Anti-Corrosion Effect of Cathodic Protection on Mild Steel Immersed Cyclically in Seawater,* Wu, J.H., Wen, X.B., Liu, G.Z., Chen G,Z., Journal of Chinese Society for Corrosion and Protection, June 1998.

[14] *Design of Seawater Ballast Tank Impressed Current Cathodic Protection (ICCP) Systems,* Lucas, K.E., Evans, M.F., Thomas, E.D., Slebodnick, P.F., Hogan, E.A., Tri-Service Conference on Corrosion Proceedings, 1997.

[15] *Guidance Notes on the Application and Maintenance of Marine Coatings,* American Bureau of Shipping, 1998.

[16] *Painting of Vessel for Salt Water Service,* Bloodgood, D.T., Steel Structures Painting Manual, Vol 1, 3rd Edition, 1994.

[17] *Marine Coatings,* Holder, A.G., Montemarano, J.A., Tri-Service Conference on Corrosion Proceedings, 1997.

[18] *Electrochemical Prevention of Corrosion and Fouling – A Review,* Gurrappa, I., Corrosion Prevention and Control, April 1996.

[19] *Marine Coatings*, Holder, A.G., Montemarano, J.A., Tri-Service Conference on Corrosion Proceedings, 1997.

[20] *Novel Non-Toxic Coatings Designed to Resist Marine Fouling*, Adkins, J.D., Mera, A.E., Roe-Short, M.A., Pawlikowski, G.T., Brady, R.F., Progress in Organic Coatings, September/December 1996.

[21] *Marine Coatings*, Holder, A.G., Montemarano, J.A., Tri-Service Conference on Corrosion Proceedings, 1997.

[22] *Marine and Offshore Corrosion Control*, Munger, C.G., Materials Performance, September 1993.

[23] *Design of Seawater Ballast Tank Impressed Current Cathodic Protection (ICCP) Systems*, Lucas, K.E., Evans, M.F., Thomas, E.D., Slebodnick, P.F., Hogan, E.A., Tri-Service Conference on Corrosion Proceedings, 1997.

[24] *Mixed Cathodic Protection Method for a Corvette-Type Ship*, Bastidas, J.M., Mateo, S.B., Mora, E.M., Material Performance, July 1998.

[25] *Cathodic Polarization Characteristics of Steel in Seawater and a New Approach for Cathodic Protection System Design*, Chen, S., Hartt, W.H., Corrosion Science and Protection Technique, January 1996.

[26] *Cathodic Protection Requirements of Ship Hull Materials*, Khambhaita, P., Tighe-Ford, D.J., Hinks, K.J., Materials Performance, February 1995.

[27] *Marine Coatings*, Holder, A.G., Montemarano, J.A., Tri-Service Conference on Corrosion Proceedings, 1997.

[28] *Painting of Vessel for Salt Water Service*, Bloodgood, D.T., Steel Structures Painting Manual, Vol. 1, 3rd Edition, 1994.

[29] *Design Considerations for Corrosion Control of Double-Hull Tankers*, Pendexter, L.A., Diettrich, D., Materials Performance, September 1993.

[30] *Thermal Spray Coatings for Marine Corrosion Control*, Brenna, R., Hays, R., Masson, R.

[31] *The Coalescence of Combustion Sprayed Ethylene Methacrylic Acid Copolymer*, Brogan, J.A., Berndt, C.C., Journal of Material Science, 32 (1997) 2099-2106.

[32] Bao, Y. Gawne, D.T., Jounal of Material Science, 29 (1994) 1051-1055.

[33] *Protective Thermoplastic Coating Specifically Designed Adhesive Polymers*, Glass, T.W., DePay, J.A., Thermal Spray Coatings: Properties, Processes and Applications. Edited by T.F. Bernecki, American Society for Metals, (1991), p. 345-351.

TABLE ONE
ABRASIVE BLASTING SURFACE PREPARATION[1]

Surface Finish	NACE No.	SSPC No.	Swedish No.	Description
White Metal Blast Cleaned	1	SP5	Sa 3	Gray-white, uniform metallic color; slightly roughened to form a suitable profile for coatings; 100% free from oil, grease, dirt, visible mill scale, rust, corrosion products, oxides, paint, or any foreign matter.
Near White Blast Cleaned	2	SP10	Sa 2 1/2	At least 95% is to appear as a white metal blast cleaned surface finish; 98% free from oil, grease, dirt, mill scale, rust, corrosion products, oxides, paint, or any foreign matter; very light shadows and streaks, and slight discoloration permitted.
Commercial Blast Cleaned	3	SP6	Sa 2	At least 67% is to be free from all visible residues, and the remainder limited to light discoloration, slight staining and light residues. All oil, grease, dirt, rust scale, and foreign matter; and almost all rust, mill scale, and old paint is to be completely removed except as permitted above.
Brush Off Blast Cleaned	4	SP7	Sa 1	Oil, grease, dirt, rust scale, loose mill scale, loose rust and loose paint or coatings completely removed; light mill scale, tightly adhering rust and paint may remain provided these areas have been subjected to the abrasive blast pattern sufficiently to expose numerous flecks of the underlying metal fairly uniformly distributed over the entire surface.

TABLE TWO
PERFORMANCE OF COATINGS[2,3]

Tank Service	Washing or Inerting	Coating Type	Number of Coats	Average Life, in years	Comments
Crude Oil Cargo Only	Flue-Gas Inerted Infrequent Water	Inorganic Zinc	1	2 to 6	Not recommended. 6 month to 2 years with sour crude.
		Epoxy	2	8 to 10	
		Coal Tar Epoxy	2	8 to 10	
		Coal Tar Epoxy	3	9 to 14	
Crude Oil Cargo Only	Flue-Gas Inerted COW and Infrequent Water	Inorganic Zinc	1	††††	Not recommended. 6 month to 2 years with sour crude.
		Epoxy	2	††††	
		Coal Tar Epoxy	2	††††	
		Coal Tar Epoxy	3	††††	
Refined Product Cargo Only	Independent Gas Inerted Infrequent Water	Inorganic Zinc	1	2 to 6	If flue-gas inerted, average life reduced to 2 to 4 years.
		Epoxy	2	9 to 10	
Segregated Ballast	Seawater Ballast	Inorganic Zinc	1	6 to 10	If post-cured inorganic zinc, average life increased to 8 to 14 years.
		Inorganic Zinc with Anodes	1	13 to 20	
		Epoxy	2	8 to 10	
		Epoxy with IOZ primer	NS	13 to 20	
		Epoxy with Anodes	NS	13 to 20	
		Coal Tar Epoxy	2	8 to 10	
		Coal Tar Epoxy	3	10 to 14	

†††† Additional data needed.

TABLE THREE
PROPERTIES OF GENERIC EPOXY COATINGS[4]

Property or Resistance	Amine Epoxy	Polyamide Epoxy	Coal Tar Epoxy
Physical	Hard	Tough	Hard
Recoating	Difficult	Difficult	Difficult
Water	Good	Very Good	Excellent
Acid	Good	Fair	Good
Alkali	Good	Excellent	Good
Solvent	Very Good	Fair	Poor
Temperature	Very Good	Good	Good

REFERENCES

1 *Guidance Notes on the Application and Maintenance of Marine Coatings*, American Bureau of Shipping, 1998.
2 *Investigation of Internal Corrosion and Corrosion- Control Alternatives in Commercial Tankships*, Ship Structure Committee, SSC-312, 1981.
3 *Tank Coating Guide for Ballast Tanks of All Vessels and Cargo Tanks of Petroleum Tankers*, SNAME Technical & Research Bulletin No, 4-23, The Society of Naval Architects and Marine Engineers, 1991.
4 *Investigation of Internal Corrosion and Corrosion- Control Alternatives in Commercial Tankships*, Ship Structure Committee, SSC-312, 1981.

International Workshop on Corrosion Control of Marine Structures and Pipelines

White Paper for Working Group on Floating Structures

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Introduction

This paper discusses the possible problems related to corrosion and corrosion protection of floating structures used for oil and gas production offshore. In this context, a "floating structure" is defined to be one of the following types of structures:

- Semi-submersible platform
- Tension Leg Platform (TLP)
- Floating Production, Storage and Offloading vessel (FPSO) and Floating Storage and Offloading vessel (FSO)
- Offshore Loading Buoy
- Spar Buoy
- Converted tankers

The paper is limited to systems and elements that are critical for safe and cost-effective operation of floating structures used for permanent production of an oil/gas reservoir. The systems and elements in question are listed in Table 1. The table also indicates which structural elements that are relevant durabilitywise for the different types of structures.

The paper describes and discusses possible corrosion and ensuing durability problems that can develop in floating structures. Furthermore, the paper points out areas for further research and development within the field of corrosion protection of floating structures.

TABLE 1:   *Combinations of type of floating structure and structural elements which may represent a corrosion problem*

Structural Element / Type of Structure	Hull	Ballast Tanks	Seawater piping	Mooring System	Turret & Thruster
Semi-Sub.	R	R	R	R	NA
TLP	R	NA	R	R	NA
FPSO/FPO	R	R	R	R	R
Offsh. Load, Buoy	R	NA	NA	R	NA
Spar Buoy	R	NA	NA	R	NA
Converted tankers	R	R	R	R	NA

R   = possible corrosion problem
NA   = not applicable or probably not a corrosion problem

Corrosion/Corrosion Protection Aspects for Floaters

Table 1 indicates different seawater exposed structural elements of different types of floaters that can present a durability problem during the lifetime or longer operational periods in fixed locations. The most important areas of concern with respect to corrosion/corrosion protection can be listed as follows:

- Corrosion of main hull/substructure
- Reliability and possible interaction effects of cathodic protection systems
- Corrosion protection of ballast water tanks
- Corrosion fatigue, e.g. of hull or mooring systems
- Localised and/or galvanic corrosion of seawater piping and fire protection systems
- Specific problems related to certain structural elements, e.g. electrical arcing damages in thruster systems, corrosion protection of turrets of FPSO's etc.

The relevance of the items listed above will of course vary between types of floating structures and from structure to structure. In addition, the climatic conditions and the environmental loads will be of significance.

Attempting to differentiate between structures, the following aspects will be of importance with respect to possible corrosion problems during service /1/ :

- Industry standard used in design and construction, e.g. shipbuilding or offshore structure procedures, or a combination of these
- Technical complexity of the structure
- Experience of construction yard
- Governmental regulations in force, e.g. maritime or continental shelf regulations
- Degree of common recognition of operational and functional requirements in design and construction between the parties involved
- Duration of operation in the same location
- Possibilities for periodical inshore maintenance work

Experience has shown that floating structures designed, constructed and operated according to generally applied and accepted offshore standards and procedures are not subject to more severe corrosion problems than normally found for fixed structures.

On the other hand, there is a significant conversion of oil tanker tonnage to FPSO's to be used in "benign" waters. These are often old ships, which have consumed a considerable part of the design lifetime, and therefore any corrosion attack on e.g. hull and ballast systems can be relatively critical. As long as this type of installation is used in mild waters for relatively short production periods, thus giving possibilities for periodical inshore maintenance and modification works, the risk of corrosion damages can be controlled. This will however require an inspection system focusing on the critical elements at regular and probably short intervals.

The types of floating structures most likely to face a durability problem due to corrosion, are those, which have, been built to different industry standards, e.g. combining offshore construction and shipbuilding practice. Of these structures, the FPSO's are the most typical and technically complex, and therefore most vulnerable to corrosion related problems of the floaters. In addition, these structures can be located for longer periods (20 years or more) in the same offshore location, and this will of course strongly affect the possibilities for maintenance and modification work in areas with limited accessibility. In this paper, the discussion of possible seawater corrosion problems on floaters is focused on FPSO's due to the arguments given above. This does not mean that possible corrosion or degradation mechanisms will not be typical or valid for the other types of floating structures

Possible Durability Problems on floating Structures Due to Corrosion

The Hull

State-of-the-art

The submerged part of a hull/substructure is corrosion protected by cathodic protection (CP) either in combination with, or without a coating system. On floaters the CP-system will normally work in combination with a high quality coating. In by far the majority of cases, the cathodic protection system is based on sacrificial anodes. However, on floaters having a ship-like hull, impressed current system is also frequently used. Some structures will also include a corrosion allowance in the structural steel dimensions.

If generally accepted recommended practices for design of cathodic protection systems of offshore structures are applied, experience has shown that this will give a reliable long-term protection of the hull. When coatings are used in combination with cathodic protection, it is important that the two systems are compatible during the service life of the structure. The coating system can degrade due to secondary effects of the cathodic protection system:

- Some coatings can deteriorate by saponification or softening due to the alkalinity produced by the CP-system
- Some coatings can loose bonding to the steel substrate due to the alkalinity produced by the CP-system
- Some coatings can blister due to hydrogen evolution on the steel substrate or due to osmotic effects

Therefore, during the lifetime the interaction effects between coating- and cathodic protection systems can cause deterioration of the coating systems. Normally, this kind of coating breakdown is accounted for in the design recommendations of a cathodic protection system and will be taken care of by increased current output from the CP-system /2/.

To withstand the aggressive conditions found in the tidal-/splash and atmospheric zones the hull/substructure is corrosion protected by use of a high-duty coating system. If the application and quality control of the specified coating system meet the requirements given in relevant coating specifications for offshore exposure, the candidate paint systems should give the required corrosion protection provided the system is maintained throughout the lifetime. The main threat to the coatings in these zones is mechanical damage.

Possible problem areas

The hull of the FPSO's is normally coated and in the submerged zone this corrosion protection barrier is supported by a CP-system. The breakdown rate of coating on the submerged part of the hull will depend upon several factors:

- Surface preparation, coating characteristics and climatic conditions during application
- Cathodic protection potential level of the surfaces to be protected
- Design and operation of the cathodic protection systems
- Lifetime requirement and possibility to perform maintenance of coating system and cathodic protection system

With respect to the first item listed above, experiences from some projects have shown that application conditions and pressure on progress can affect the obtained coating quality significantly /1/. Many hulls for FPSO's have been built in shipyards which have previously not been used to, or trained to meet specifications and expectations generally applied in the offshore construction business. In shipyards generally, the surface preparation and coating work require extensive verification and control, and for FPSO hulls the amount of work (on 24 hours basis) makes this activity difficult to fulfil. In addition, many of the yards engaged to build the hulls are

located in regions where the climatic conditions, e.g. with respect to relative humidity and rainfall, are such that the required quality can be difficult to achieve. This can be compensated by the use of climatically controlled painting halls, but due to tight time schedules and necessary joining of modules, some outdoor surface preparation and coating works will take place. It may therefore be questioned if the coating system applied on the hull has the quality normally required for permanently installed offshore structures.

Possible breakdown of the coating system of the hull during service will, as previously mentioned, depend upon the characteristics of the cathodic protection system. The hull of an FPSO will normally be protected by an impressed current system, possibly in combination with sacrificial anodes to secure protection locally, e.g. in sea chests. It is normally considered that a coating system should not experience a protection level more negative than −1050 mV vs. Ag/AgCl (seawater) reference electrode to minimise the possibility of softening, blistering or disbonding of the coating during service. With an impressed current system, a more negative protection level can develop locally on the hull. This will depend upon the operation of the impressed current system. Normally these are automatically controlled systems where recordings of anode hull potentials control the current output of the system. However, the protection potential gradients found on the hull will depend upon distribution geometry of impressed current anodes, the numbers of impressed current anodes and the number and location of potential recording reference electrodes. "Overprotection" of the hull locally, presumably in areas close to the impressed current anode, can be counteracted by the use of dielectric shields around the anodes.

Even though the track record of impressed current systems on ships have been mixed, it is considered that the "high quality" systems applied on the hull of the FPSO structures should be considered adequate /3/. The long term reliability will, however, depend upon many factors, such as:

- Type of impressed current anode used
- Stability and location of reference electrodes
- Quality of cable penetrations
- Mechanical protection of impressed current anodes
- Stability of dielectric shields
- Integrity of cable insulations and insulation of impressed current anodes

A required long-term operation of the impressed current system will require close follow-up during the lifetime. A system working outside the predefined operational limits can cause significant damages both with respect to loss of corrosion control and accelerating coating breakdown.

Normally impressed current system will be controlled potensiostatically within pre-set potential limits. When such a system is operating on installation equipped both with sacrificial anodes and a high quality coating system, attention should be given to operational conditions of the total system. On some FPSO's, the impressed current system will start to provide current when the pre-set potential level at the hull area most far away from the impressed current anodes show a potential level more positive than -800 vs. Ag/AgCl reference electrode. Prior to this, the hull

will be protected by the sacrificial anodes leaving the impressed current anodes unenergised. If this situation prevails for longer periods, the characteristics of the impressed current anodes can be affected. E.g. marine growth can settle on the impressed current anodes, and this can give attack on the anode material when the anode starts operating. Some impressed current anodes, e.g. lead-antimon-silver based materials, need a minimum current density to ensure the passivity of the material. If the impressed anode is working at lower current densities, an increased consumption rate and shorter lifetime can be expected.

On other FPSO's more negative potential levels have been applied as the controlling one for impressed current systems. This has in some cases given the effect that all or some of the sacrificial anodes have been cathodically protected and acting as "sleeping" anodes. When activation of the anodes is required, the "sleeping" prehistory can influence the ability to deliver current. This could affect the long-term behaviour of the total corrosion protection system, and should be considered both in the design and operational phases.

Discussing the interplay between separate elements in a hybrid cathodic protection system it should be mentioned that computer modelling could be an effective tool revealing possible problems of either under- or overprotection given by a specific design. Computer modelling could also give valuable design input on the sizing of dielectric shields, optimising the number and location of both sacrificial and impressed current anodes and the possible long-term effects of coating breakdown and reference electrode instabilities.

Another uncertainty that should be considered is the interplay between the impressed current system and the applied coating system. Even though there are many successful examples of coatings in combination with cathodic protection, these are mainly based on sacrificial anodes as the CP-system. This combination is probably potentially less harmful to the coating system than that of an impressed current system. Long-term experience with the combination of coatings and impressed current systems is lacking, and the relevance of standardised qualification testing to characterise field service behaviour can be questioned. In order to develop an understanding and a model of the coating breakdown mechanisms during the lifetime of an FPSO, more work is needed.

In the tidal/splash and atmospheric zones of the hull a coating system will be the only corrosion protection. The coating systems will normally be organic type coating systems with a dry film thickness higher than 300 – 500 μm /3/. In all zones above the water line the coating will degrade during the lifetime, and in addition the coating system can be subject to mechanical damage, especially in the tidal/splash zone and on deck areas. In some recommended practices, e.g. NACE Standard RP-0176-83 /4/, it is expressed that an organic coating system cannot be considered to give permanent protection in this zone. Consequently, the need and possibilities for offshore maintenance work have to be considered. On a short-term basis, lack of maintenance will probably not affect the structural integrity of the structure. In a relatively long lifetime horizon, an ad-hoc based attitude to coating maintenance can turn out to be both expensive and detrimental to the integrity of the corrosion protection system. A regular condition assessment of the coating system should therefore be the basis for a planned maintenance activity. How to perform coating maintenance offshore, is still an area, which has possibilities for significant developments, improvements and optimisation.

Ballast tanks

State-of-the-art /5/

Severe corrosion can often be experienced in the seawater exposed internal compartments of a hull. Especially in the ballast tanks the corrosivity can be extremely high resulting in corrosion attacks threatening the serviceability of the ship/floater. A corrosion attack on the structural steel of the hull can also enhance a possible fatigue problem relevant for some structures, e.g. FPSO. The reason for the high corrosivity is a result of the exposure conditions found in the ballast tanks, which can be characterised by the following:

- Alternating exposure to seawater/marine atmosphere as the tanks are filled/emptied
- Sloshing and washing as a result of movements of the installation
- Varying temperature as a result of heating/cooling of the atmosphere, heating from cargo tanks, engine rooms etc.
- Highly stressed areas

Normally tanks permanently or intermittently exposed to salt-water ballast are corrosion protected by a coating system supported by a sacrificial anode based cathodic protection system. The coating system can be of varying quality, ranging from one-layer systems with a typical thickness of 200 $\square$m to two or three layers systems with typical thickness of 400 $\square$m.

Experience has shown that ballast tank coatings often have a shorter lifetime than expected. In practice a lifetime scatter from a few months to more than 25 years has been found. The main reason for the poor behaviour of some systems are:

- Inadequate specification of the coating system and the steel surface preparation
- Lack of coating technology knowledge
- Insufficient follow-up of surface preparation and application work
- Unfavourable exposure conditions
- Interfering work, e.g. welding and other mechanical work during and after the coating process

The exposure conditions found in ballast tanks are such that the general ageing mechanisms of the coating system are aggravated. A significant contributing factor to coating degradation is the increasing brittleness and loss of flexibility with time, causing cracking and disbonding at structural hot spots. The coating system may be flexible enough when newly applied and a few years thereafter. Then, due to cyclic temperature variations, the more volatile, low molecular weight coating constituents are lost by evaporation or washed away by the ballast water. Oxidation and other chemical changes of the coating constituents further contribute to the gradual loss of flexibility.

The tendency to loss of flexibility of coatings depends on the type and quality of its constituents, e.g. raw materials such as binders, extenders and flexibilizers, pigments etc.

Taking into consideration that the coating system in a ballast tank can degrade relatively fast, special consideration should be given to the parts of the tank which is difficult/impossible to protect cathodically. E.g. during non-ballast periods shallow layers or pools of water may remain on the tank bottom possibly causing local corrosion attacks. Also in the top of the tank special conditions can develop. In this area stress and temperature variations can be relatively high, giving accelerated breakdown of the coating system. In such a situation the cathodic protection system will give protection only when the ballast water is reaching the tank ceiling.

In order to secure the integrity of the installation, the coating system of the ballast tanks must be carefully maintained, especially in areas where the cathodic protection system is not giving continuous protection.

Possible problem areas.

On FPSO's the ballast tanks are located around large cargo tanks, which are continuously holding the produced oil/gas. The produced hydrocarbons can have high temperatures (up to above 100 $\square$C) thus serving as a very efficient heating reservoir for the ballast tanks. Consequently, large temperature gradients can be found in the ballast tanks of floating production and storage units. These gradients can enhance the corrosion aggressiveness of the seawater in the tanks as well as giving optimum conditions for bacterial activity and resulting corrosion attacks locally. The more severe conditions found in this type of ballast tanks will also put more strain on the applied coating system. The coatings must withstand repeated temperature cycling. This requires coating system that remains flexible and a resistance to brittleness during the lifetime. Within the coating industry there is a significant lack of information on how the flexibility of the coating is affected by ageing. More data is highly needed in this area. In this respect it should be mentioned that Marintek in Norway has developed a laboratory test method to qualify ballast tank coatings, which involves the use of the following two test methods:

- Wave tank (simulating real ballast tank conditions)
- Condensation chamber

The wave tank is a tank with natural seawater of 35 $\square$C and room for 4 test panels. The test panels are one deck panel, one side panel with cold wall effect (temperature gradient about 15$\square$C), one side panel without cold wall effect and one bottom panel with zinc anode. The tank has wave movement to achieve splash of seawater and it has temperature heating by radiation on the deck panel (alternating 12 hours 50 $\square$C/12 hours room temperature). The test cycle is 2 weeks with seawater and wave movement and 1 week with seawater below the bottom panel and no wave movement. The condensation chamber is a chamber in which test panels are exposed to continuous condensation, which may accelerate moisture penetration and possible blister formation.

In the testing, coatings can be tested on substrates with different surface condition, e.g. ranging from blast-cleaned to pre-rusted/moist steel surfaces. In this respect the effect of the surface condition prior to the coating application can be taken into account. Based on the test results, mainly blister density and area rusted, a classification system ranking different coating systems

has been worked out. Both for manufacturers and users of ballast tank coatings, results from this type of testing can give valuable input on the durability of specific systems.

Another aspect with regard to the coating system that has to be considered, is the requirement to elongation. Coatings applied on relatively high strength steels should have the capacity for adequate relative elongation to withstand increased strains and movements found in installations built from such steel. Long-term flexibility will therefore be important, and this property should be considered and documented for the applied coating systems.

Also for ballast tank coating systems in permanently installed floating structures there is a need to develop maintenance procedures to secure the long-term protection of these vital parts of the hull. In addition there is a need to develop understanding, inspection- and test methods that reliably reflects the long term behaviour of coatings to be used in ballast tanks.

Mooring systems

State-of-the-art /6/

Floating units used for oil and gas production are positioned by use of a mooring system. The following main categories of mooring system are applied:

- Tension leg mooring
- Taut mooring
- Catenary mooring
- Single point mooring

Tension leg platforms (TLP) use primarily tubulars for tension mooring. The applied materials for the tubular are high quality C-steels with relatively high strength. The major concerns with respect to corrosion are stress corrosion cracking or corrosion fatigue. These mechanisms are normally counteracted by use of cathodic protection in combination with a coating system. Several tension leg platforms have used thermally or flame sprayed aluminium as coating system for the tension leg tubulars.

The experience with the use of tubulars in a tension mooring system has been generally good, and no specific experiences related to unforeseen corrosion activity have been reported.

The other three mooring systems listed above can consist of:

- Chain links
- Steel wire ropes
- Fibre ropes

either individually or in combinations.

Chains are most frequently used for mooring lines. The chain links are normally not provided with any corrosion protection other than a dimensional corrosion allowance. The required dimensional addition can vary, depending upon exposure zone, inspection intervals and body/ society specifying the requirement. The Norwegian Petroleum Directorate requires 0.8 mm/ year addition for chains to be used in the tidal/splash zone while DNV require 0.4 mm/year for chains not subject to periodical surveys. These differences may reflect differences in the evaluation of the corrosion loads on mooring chains. One aspect that is frequently discussed is the effect of marine growth on chains. For such components, which are designed with a corrosion allowance, the settlement of biofouling can be beneficial by limiting the supply of oxygen to the metal surface. This limited oxygen transport will reduce the corrosion rate. On the other hand, however, the putrefaction and by-products of marine fouling and organisms can be detrimental to the substrate steel material. This can give localised corrosion attacks possibly affecting the integrity of the complete chain link. It is also possible that marine growth can create different microenvironments on the steel surface, e.g. both aerobic and anaerobic areas. This can give differential aeration cells, where the area of lower oxygen concentration will be anodic to the area with more ample oxygen supply.

Even though chains are relatively tolerant to general corrosion, corrosion induced failures have been experienced.

The following mechanisms seem to be the most critical:

- Corrosion fatigue
- Bacterially induced corrosion
- Embrittlement due to corrosion in acidified or anaerobic environments.

Even though corrosion protection of chains is not commonly applied, this can be considered for chain based mooring systems of floating structures installed for long-term operation in one location. The following methods should in principle be applicable:

- Use of corrosion resistant alloys
- Cathodic protection e.g. by sacrificial anodes distributed along the mooring line
- Application of a metallic coating, e.g. such as aluminium on individual chain links

The two latter methods are probably the easiest to implement. However, the high strength steel qualities used for chains are susceptible to hydrogen induced cracking.

Steel wire ropes are also applied in mooring lines. When exposed to seawater, the rope can be protected against corrosion by different methods:

- Metallic coating of individual steel wires
- Filling the annulus of the rope with grease/wax to avoid water ingress
- Include a sacrificial anode wire in the rope to provide "internal" cathodic protection
- Install the rope in a non-metallic sheath and thereby establish a barrier between the steel material of the rope and the seawater

The long-term experience with wire rope mooring lines is relatively limited. The failures experienced are mostly related to mechanical damage during anchor installation and handling.

Wire ropes used for long-term mooring purposes are normally mounted in plastic sheathing to give additional corrosion protection. For these ropes epoxy potted terminations have been applied. More frequently zinc is used as potting material.

For deepwater mooring purposes different synthetic fibres are also candidate materials for ropes. The most commonly applied materials are:

- Nylon
- Polypropylene
- Polyester
- Aramid

Experience with the long-term behaviour of these materials in seawater has not yet been gained, but factors such as the following must be considered when applying these materials in mooring lines:

- Surface wear
- Environmental impact of seawater and seamud
- Fatigue, torque and internal abrasion
- Biological degradation

Possible problem areas

For chains applied for long-term mooring purposes the following items should be given further attention from a corrosion point of view:

- Susceptibility of different chain steel grades to hydrogen embrittlement
- Degradation mechanisms induced by bacterial corrosion activity
- Possible corrosion fatigue problems driven by the trend to a higher utilisation of the strength capacity of the chain

For steel wire ropes the following aspects should be brought into focus:

- If the external corrosion protection barrier (sheathing) is damaged, will the rope be susceptible to possible hydrogen embrittlement effects?
- For the terminations where epoxy has been applied as potting material, can ageing and creeping of the epoxy affect the integrity of the mooring line?

For fibre ropes one of the main issues to be addressed is to evaluate the possible effect of particles entering the rope construction. Particles can give abrasion in the rope, thereby reducing the fatigue life of the mooring line.

The environmental impact and ageing characteristics of fibre materials used should be considered for mooring systems with life times more than 15 –20 years.

Seawater piping systems

State-of-the-art

The materials used in seawater piping systems on floating structures will vary. The following types can be found /7/:

- Carbon steel
- Coated carbon steel
- Copper-nickel
- Stainless steel
- Glass reinforced plastics or epoxies (GRP/GRE)
- Titanium

When the above mentioned types of seawater piping systems have been produced to normal offshore specifications and requirements, the corrosion problems experienced will not be significantly different for fixed and floating structures.

One area that has been focused in recent years is the fabrication quality of the piping systems found in FPSO's. This is an area where yards primarily with shipping experience are facing stricter offshore requirements. For low-pressure systems made of carbon steel, however, the fabrication quality seems generally acceptable. For higher quality materials, such as stainless steels and titanium, the fabrication quality has been more questionable. On some projects extensive welding repair work had to be performed on the seawater piping prior to operation start-up. The relative marginal welding quality of the seawater piping found on some FPSO's may raise concern that this will give increased problems due to corrosion during service.

Also for GRE/GRP piping problems have been identified on some field performed glued joints. Due to the lack of quality in the field joints, a procedure to add a GRE laminate externally on the joint has been adopted /1/.

The quality of cast stainless steel piping components should also be addressed. It has been experienced that improper heat treatment can give a significant reduction or total loss of the expected corrosion resistance. This is due to the formation of intermetallic phases during the heat treatment process.

If quality deficiencies such as those generally described above are present, corrosion problems will probably occur during service if no protective measures such as cathodic protection are taken. On an FPSO the conditions can be such that the general corrosion problems inherently present in seawater will be aggravated due to environmental conditions found e.g. in the ballast tanks. The temperature of the ballast water can be relatively high due to the heating from the storage tanks. The external seawater temperature of the ballast water piping can then be close to

or higher than the critical crevice/pitting temperature for the applied stainless steel grade. It has been reported that the metallic continuity of the piping systems in some ballast water tanks has been lacking. This means that individual items will not be cathodically protected. Consequently, these parts must externally withstand the relatively corrosive environments found in the ballast tanks.

Internally, the topside seawater piping will be exposed to chlorinated seawater. The chlorination will increase the risk for corrosion initiation on stainless steels because the free potential will be raised positively. On the other hand, the cathodic activity will be lower in chlorinated seawater due to the loss of biofilm activity, thus the propagation rate will be lower than in untreated seawater.

If the welding quality of the highly alloyed seawater piping used on FPSO's is substandard, corrosion attacks must be expected during service. This can be prevented if a cathodic protection system is installed.

Possible problem areas

For highly alloyed seawater piping systems one of the main problems is to get matching seawater resistant materials for all parts included, e.g. such as valves and pumps. Certain components, such as springs, metal to metal seals and sterns, require high strength and are therefore often produced from other materials than the corrosion resistant material applied in the main line. The documentation of the seawater performance of the different high strength materials used is often limited.

As previously mentioned, cast components can represent a possible corrosion problem. Larger dimensions are difficult to cast without cracking. Welding of cast components is also a problem. In addition, heat treatment can also be critical due to the possibility of formation of intermetallic phases.

As discussed above, there is a multitude of materials and different qualities of the same material in a seawater piping system. Due to this, extensive corrosion has been experienced after only short exposure periods on some platforms. Some operators attribute many of these failures to insufficient material qualification procedures. There is therefore a need to establish reliable, reproducible and commonly accepted crevice corrosion test to qualify stainless steel (and nickel alloys) for use in seawater. The establishment of testing procedures to qualify high alloyed materials for marine applications, will make it possible for suppliers and users to test the materials and products on a common and more reliable basis. This should lead to a better conformity between in-service behaviour of materials and products and results obtained through testing. This could mean reduced rate of service failures and thus reduced loss of production. Within the European Federation of Corrosion (EFC), work is presently undertaken to develop testing guidelines to qualify stainless steels for application in marine environments.

Other components

Turret system

The turret system is an integrated part of a FPSO and allows the ship to rotate when the weather situation requires this, or when compensation for twisting in the anchor lines is needed. The turret accommodates the riser manifold, the mooring lines and the swivel joint or dragchain. The turret itself is a mechanically complicated installation consisting of a roller/bearing arrangement in combination with a system for rotation and locking. The turret will be partly submerged, thus facing both marine atmosphere and seawater.

The corrosion protection of the turret is normally based on a combination of a coating system and sacrificial anodes. The major uncertainty with this system is whether all parts of the turret system are in proper metallic contact and thereby properly cathodically protected. If not, the parts of the turret not experiencing metallic continuity with the sacrificial anodes will possibly corrode freely as the coating system degrades during service. It is therefore important to perform potential surveys locally in the turret area to reveal possible lack of corrosion protection of some parts.

Normally the turret is galvanically coupled to the hull of the ship. Consequently, the turret will also drain current from the CP-system of the hull. If this is an impressed current system, there is a possibility that the submerged parts of the turret can be cathodically polarised to relatively negative potential levels. All materials used in the different parts of the turret should therefore be evaluated in relation to possible embrittlement tendencies as a result of hydrogen uptake. This consideration should especially be given to any high strength materials applied, e.g. in special parts such as bolts etc.

Also in the atmospherically exposed part of the turret the integrity of the corrosion protection system should be controlled and maintained. In shielded and poorly accessible areas this is important as the corrosivity of the marine atmosphere present locally can be high.

Stray current effects on thrusters /8/

An FPSO is normally equipped with a thruster system, which keeps the vessel against the weather and allows the ship to turn. Thruster breakdown has been experienced already during transfer from the shipyard to the hydrocarbon production location.

A failure analysis of the case concluded that the breakdown was caused by a mechanical fracture of the pinion teeth. In addition, a transfer of metal due to electrical stray currents within the thruster was observed. This arcing effect was not, however proved to be the reason for the observed failure.

Also on other vessels observations have been made indicating the presence of arcing effects on the thruster system. It is, however, too early to conclude that the electrical arcing will give breakdown of the thruster gears, bearings and the shaft. However, the arcing effects are

undeniably of importance, as they introduce a possible weakening of the thruster system with consequential failures as a possibility.

Normally, arcing effects on propeller systems are counteracted by fitting a slip-ring to the shaft and secure grounding to the main hull via a bonding brush. However, the bonding brush will become worn and the grounding to the hull will be lost. For the thruster units, it is very difficult to change the bonding brush due to accessibility restrictions. This will give a metallic discontinuity between the hull and the thruster unit during service.

In order to prevent the thruster units from arcing effects, the preventive actions must comprise an understanding, elimination or control of the stray current effects present. So far, the origin of the stray current has not been concluded. However, currents induced by the cathodic protection system have been put forward as one explanation. The potential difference between the propeller normally made from NiAl Bronze and the cathodically protected hull may be large enough to give electrical arcing. Theoretical considerations and literature studies support this assumption. If this is correct, the design philosophy regarding cathodic protection and/or the design of thrusters for cathodically protected FPSO's must be revised.

DNV in Norway, in co-operation with the industry has started work to validate or eliminate the hypothesis that the cathodic protection system is the origin of harmful currents. The project will be completed during 1999.

Summary/Conclusions

Floating structures used for exploitation of hydro-carbon reservoirs offshore, should in general not be subject to more extensive corrosion than fixed structures when typical offshore requirements to design, fabrication and operation have been applied.

The main corrosion challenge for floaters will be found on structures on which production, processing and storage of hydrocarbon are taking place. These structures offer a combination of a ship's hull as substructure and an offshore topside processing plant as deck structure.

These floaters have been designed and built both according to standards and procedures common for the shipbuilding industry (the vessel itself) as well as to standards and procedures common to the offshore construction industry (the topside facility). As a consequence of this, the quality level of some systems may therefore be somewhat lower than that typically found on an offshore structure. As these floaters also will be located in the same position for many years without possibilities for periodical inshore maintenance work, a progressive durability problem due to corrosion and material degradation can develop. The most important aspects recommended for future research discussed in this paper are the following in order of priority :

1   The ballast tank environment will be very aggressive to the corrosion protection system, and especially the coating.

Temperature fluctuations and varying strain and movements of the steel substrate will require high flexibility and low tendency to embrittlement of the coating. These properties are presently not very well documented for ballast tank coatings, and more data are needed to understand and document the ageing properties of coating system candidates.

2   With respect to the external corrosion protection of the hull the long-term ageing and breakdown characteristics of the applied coating system working in combination with an impressed current cathodic protection system is not very well documented, and tests designed to provide such data seem to be of limited relevance.

The long-term operation of the CP-system within safe and predefined limits is also a challenge with respect to an even current and potential distribution throughout the lifetime.

3   For the mooring systems data on long-term behaviour of different types of mooring lines are scarce and work should be initiated to document this better.

For chain links the aspects needed to look into, embrace possibilities for bacterially induced corrosion, the possibility for corrosion fatigue of highly stressed systems and the possibility for long-term embrittlement effects on links either directly cathodically protected, or draining current from the CP-system of the substructure.

For steel wire ropes the long-term reliability of the corrosion protection system should be documented especially with respect to any sheathing acting as a barrier against seawater ingress and the consequence of seawater ingress on hydrogen embrittlement effects.

For fibre rope systems there is a general need to document the long-term behaviour in seawater.

4   The high alloyed seawater piping on some floating production units built during the last years can give rise to a corrosion problem because the welding quality may be slightly substandard in relation to normal offshore specifications. In addition, the seawater piping may include components made from alloys not matching the corrosion resistance requirement of the main line.

The seawater piping in the ballast tanks may be exposed to an environment more aggressive than anticipated at the design stage.

There is a need to establish testing procedures which, in a reliable, reproducible and commonly accepted manner document and qualify the corrosion behaviour in seawater of different materials and components.

5   The arcing effects found on thruster systems due to stray currents must be examined and understood in order to specify preventive actions.

References

/1/   Alfstad, O.: "Norne, Varg og Åsgard", paper at NIF conference Flytende produksjon offshore, Sandefjord, October 1998 (in Norwegian).

/2/   DNV Recommended Practice RPB401, Cathodic Protection Design, 1996.

/3/   Strandmyr, Ø.: "Materialfilosofi for Norne Prosjektet" paper at conference Materialteknologi for Petroleumsindustrien, Trondheim, January 1996.

/4/   NACE Standard RP0176-83, "Corrosion Control of Steel, Fixed offshore Platforms Associated with Petroleum Production", 1983

/5/   Askheim, E.: "Ballast Tanks & Cargo Holds in DNV's Guidelines for Corrosion Protection of ships", PCE, June 1997.

/6/   Salama M. M.: " Materials for Mooring Systems", Chapter 8 in Treatise on Materials Science and Technology, Volume 28, Academic Press Inc., 1988.

/7/   Mollan, R.: "Experiences with 6Mo Stainless Steel Offshore in the North Sea", European Federation of Corrosion Publications, Number 19, The Institute of Materials, 1996.

Corrosion Protection of Fixed Offshore Structures

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1.0   ABSTRACT

Although corrosion protection of fixed offshore structures has been long established, it is an industry that has yet to reach maturity. Opportunities do exist for improvements and reduction in cost in the application and control of corrosion protection of both new and existing structures. For new structures, and deep water development a radical reduction in corrosion protection costs will require revolutionary advances in materials of construction, cathodic protection systems and coating technology as well as improved management systems to ensure design, procurement, fabrication, installation, inspections, tests and preventive maintenance requirements are met.

2.0   INTRODUCTION

Fixed structures have been the foundation of the offshore petroleum production industry since its inception. In recent years the use of fixed structures has been extended to water depths of over 400 meters. For the purposes of this paper, it will be assumed that this water depth may be at or beyond the economic limit for future fixed structures, as great improvements are being made in the design and reliability of subsea production systems. Corrosion protection of fixed offshore structures and Jackup rigs operating as fixed structures, include a number of methods used for various corrosion protection applications found on three primary structural elevations: above water structural components from the +15 foot elevation up to the deck level. The splash zone from –15 foot elevation to + 15 foot elevations and below water from –15 foot to below seabed elevations. Corrosion protection of components found above the deck level are not addressed in this paper.

In general there are a number of ways to approach corrosion control. Primarily, **Cathodic protection** is the basic method now used for below water protection of offshore structures. **Organic and metallic coatings** are being used to a greater extent in conjunction with cathodic

1

protection from the –15 foot elevation to the deck elevations. Changes in **materials of construction** are a long-term prospect. **Changing the environment** or **changing the process** seem to have little application to corrosion protection but have direct bearing on the selection of anode materials, monitoring, inspection and testing activities. Changes in structural design and in design philosophy may also impact the corrosion control system and re-enforces the importance of management of change programs.

Once a corrosion control strategy has been adopted, it is necessary to develop and or follow quality assurance program requirements to ensure that the overall strategy meets its intended objectives during procurement, fabrication, installation, and or retrofitting. A program for monitoring and maintenance of the system is also a key component for any CP system to be effective. In addition a proactive approach to controlling deficiencies found during routine monitoring and inspection needs to be established to optimize performance.

3.0   CATHODIC PROTECTION

Cathodic protection has been successfully used nearly from its introduction to protect the industry's offshore capital investment from corrosion. There are operating structures in the Gulf of Mexico which have been exposed to corrosive sea water for over 50 years. Although much knowledge has been gained about the successful application of cathodic protection, no generally used detailed model of the CP process and its resulting polarization exists. There is industry alignment in-so-far as current Density (ref NACE RP 0176 (1994) and DNV RP B401). However, company's are not aligned in calculating surface area and coating deficiencies. Calculation criteria varies from company to company and between engineers within companies (e.g. Company "A" may calculate surface area of all steel in the water column as exposed surface. While Company "B" may exclude such components as boat bumpers, pilings, and other items considered secondary.) In spite of this, the practical application of CP has been well established.

Considering the long history of success and fine tuning of CP for steel structures, it is likely that radical improvement in the economics of corrosion protection for new construction will require a revolutionary change in materials of construction and or in the methods of application of CP. There is considerable room, however, for evolutionary improvements such as improved quality assurance, monitoring and maintenance that can reduce overall CP costs considerably in both new construction and retrofit of existing structures.

3.1   Regulatory Requirements Regarding Cathodic Protection of Fixed Structures in The UK Sector of The North Sea

The basis of the British health and safety law is the Health and Safety at Work etc Act 1974.
In his report on the Piper Alpha disaster in the UK sector of the North Sea, Lord Cullen recommended the introduction of a safety case regime offshore, underpinned by complementary legislation dealing with specific aspects of safety. The key new sets of offshore regulations made under the HSW Act with direct relevance to the CP system are:

i)   The Offshore Installations (Safety Case) Regulations 1992 (SCR)

ii) The Offshore Installations and Wells (Design and Construction, etc) Regulations 1996 (DCR)

The replacement of the old prescriptive regulations with more modern goal setting regulations resulted in the requirements concerning monitoring, inspection and testing of Cathodic Protection (CP) systems and coatings becoming implicit in the high level goals set out in the regulations. This provides the duty holder with considerable freedom in making suitable arrangements to comply with the regulations.

Under sections 2, 3, and 4 of Health and Safety at Work Act 1974, the duty holders are required to ensure so far as is reasonably practicable the maintenance of a place of work in a condition that is safe. An offshore installation is considered to be a place of work and hence maintenance of its integrity is an implicit requirement.

These general requirements are supported by the Offshore Installations and Wells (Design and Construction , etc) Regulations (SI 1996/913) (DCR) which require that the installation is designed, constructed, operated and decommissioned such that as far as reasonably practicable, integrity is ensured. In particular regulation 5(2)(b) requires due account to be taken of processes that could cause significant degradation of material properties and the means by which they can be prevented. The installation CP system is one of the means of preventing degradation due to corrosion. Requirements for periodic assessment of the installation integrity (reg 8) can be interpreted as including an assessment of the CP system and its effectiveness.

DCR also introduced into the SCR a requirement for all installations to have in place a written scheme undertaken by Independent Competent Persons, to verify that its safety critical elements are suitable and remain in good repair and condition throughout the lifecycle of the installation. The CP system is considered to be included within the scheme and as such would be subject to verification. Amongst matters to be provided for in the verification scheme there is a need to define the nature and frequency of examination and testing and the need to produce and preserve records of examination and testing carried out, the findings, remedial action recommended and the remedial action taken. The actual techniques to be used for the testing/examination would be subject to agreement between the duty holder and the independent competent person.

A recently completed inspection project by HSE revealed that generally an initial baseline evaluation of the CP system is undertaken after the jacket is installed. Thereafter, inspection strategies vary although the majority still tend to revolve around five year inspection programme. Failures in sub-sea parts of the installation have been dominated by fatigue and hence corrosion monitoring and evaluation of CP systems usually receives less attention (once or twice in a five year period.). Survey of CP potentials is usually carried out by divers or ROVs.- use of permanently fixed monitoring systems being limited to a few installations. With many structures exceeding their original design life (up to 30 years of service) it is appropriate to consider the possibility of enhanced risk of corrosion and the need to assess the effectiveness of the CP system.

3.1 Design Parameters

The development of the rapid polarization concept has lead to increased emphasis on the current density achieved on a cathodically protected surface as a function of time. As early as 1948, it was noted that maintenance currents were covered when initial polarizing current densities were high (ref. F - 9). This was attributed to a denser, more protective calcaneous deposit formed under high current density conditions. Many studies have now been published showing that the actual current density on a well polarized steel surface is significantly lower than the value that has been assumed in the past based on anode consumption rates and on laboratory measurements of anode efficiency. The only way to reconcile observed anode life with these low current density measurements is to reduce the anode efficiency, often by a factor of 2 or 3.

Although the laboratory quality assurance tests for sacrificial anode materials are explicitly not intended to predict field performance, the corrosion engineer often has no other data to draw on. As design life is extended, it becomes more important to know actual efficiency to achieve the most economic designs which meet design life. Some data have been published on the efficiency of particular alloys based primarily on laboratory testing, but no general data base exists on anode performance in the field as a function of alloy composition, temperature, and anode current density.

The application of new concepts such as the design slope parameter method to design of offshore structure CP simplifies the design. Adoption of this design method will to some extent depend on its incorporation into industry standards over the next few years.

3.2 Impressed Current Cathodic Protection

It has long been recognized that impressed current systems for offshore structures could offer certain advantages (i.e. lower weight, adjustable current output) over sacrificial anodes systems. Unfortunately the impressed current systems that have been installed have had limited success resulting in a negative attitude towards the use of impressed current systems offshore.

Failures of the early impressed current cathodic protection systems can generally be classified into 4 categories (1) component failure, (2) operational shortcomings and (3) lack of monitoring and maintenance (4) design specification / installation issues. Component failures were typically associated with the cables, the anodes and the supporting hardware. Failure of the anode to cable connection and damage to the cable in the splash zone was common. Modern impressed current anode designs have to a large extent mitigated lead wire failures by encapsulating the connection point, and by improvements in the electrical insulation applied to the lead wire. Failure of lead wires passing through the splash zone continue to be a problem, although designs which use heavy wall pipe as conduits seem to be more robust than earlier designs. Replaceable systems have not proven reliable. Operational problems were typically related to uneven current distribution resulting in some areas being overprotected while other areas remained underprotected. Monitoring and maintenance of offshore impressed current systems was typically lacking. Operators more concerned with production activities are expected to maintain systems they are unfamiliar with. Often times the systems became de-energized and remained so for extended periods of time. There have been cases where operators have de-energized a

cathodic protection system because it was thought to have caused interference problems with computer systems and TV reception on the platform. . Design failures include, for example, improper location of impressed current anodes during the design or installation phases. Location points should be analyzed carefully to include interference with pipeline areas that can become a problem (ref. Section 8 - Quality Assurance)

In the last few years a limited number of impressed current cathodic protection systems utilizing mixed metal oxide anodes have been utilized for retrofit systems. The anode strings are attached to a steel cable which is tensioned between the platform below the water level and a clump weight on the sea floor. These systems incorporate changes in both the materials and the design to improve the reliability. Such systems have been installed in the Gulf of Mexico, off the west coast of Africa and in the Caspian Sea. These systems have shown potential but no long term data is available.

Published costs indicate that the cost of an impressed current system using the tensioned anode strings is approximately 50 percent the cost of retrofitting with a sacrificial anode system.[ref. A - 1] These costs were developed for a twenty year design life on an 8 pile platform in 160 feet of water in the Gulf of Mexico. Because of minimal diver involvement with the impressed current system, the cost savings could be greater for platforms in deeper water where dive costs are significant.

4.0 ORGANIC COATINGS

On pipelines and onshore equipment, coatings are widely used in conjunction with cathodic protection in order to reduce current demand and improve current distribution. On offshore structures current distribution is generally not an issue due to the high conductivity of sea water and the ability to mount anodes physically near all parts of the structure. Reduction in current demand, however, translates directly into reduction in the weight and therefore cost of sacrificial anodes. Coatings have not generally been used to date below the -15 foot elevations for shallow water structures, primarily for economic reasons.

For example, cathodic protection in relatively shallow water offshore (Gulf of Mexico) using aluminum sacrificial anodes costs roughly $0.08/ft^2$/yr (installed cost) for a bare steel structure. Shop application of a good quality coating to steel tubulars used in the construction of conventional structures costs about $2.00/ft^2$. (Application costs for random shapes and for weld line coating in the fabrication yard can be considerably higher.) So for coating to be economical for offshore structures, design life must exceed 25 years even assuming a perfect coating with no degradation. A coating which suffers significant degradation (> ~10% mean breakdown) gives almost no economic advantage, except in special circumstances where the amount of anode material must be limited.

The situation may be quite different in moderate and deepwater installations. Weight considerations for fabrication designs and installation procedures may make organic coatings a more attractive option than a massive anode payload.

The rate of coating degradation in the marine environment is not well known. Recommendations in DnV Recommended Practice B401 are known to be very conservative, but are the only values available to most CP designers. However as depth increases the use of coatings becomes a more viable option. The use of the DnV numbers makes coating of offshore fixed structures not economically viable in most cases. Improvements in coating degradation models and increased system design life to 30 years or more may make coatings look more attractive

A detailed discussion of organic coatings corrosion protection for fixed offshore structures is beyond the scope of this document. Important details are available from various sources (ref. B – 1 through 4). Use of organic coatings below the –15 foot elevation is subject to economic considerations pertaining to cathodic protection designs. However, the region between the –15 foot elevation and the deck level must be protected by alternative methods including organic coatings. Surface preparation is very important and certain coating types may require specific treatments. In some cases, only white metal blasting may satisfy the coating supplier's requirements. For the splash zone (wet/dry tidal region), mechanically robust systems must be used such as high-build coatings. In the atmospheric zone, a wider variety of protective coatings can be used including wash primers, zinc-rich primers, organic inhibitive primers, topcoats of chemically-cured, solvent deposited or thermoplastic types, and antifouling coatings. Compatibility of these materials must be carefully considered to avoid large-scale coatings failures.

5.0   METALLIC COATINGS

Metallic coatings have been applied to the highly-corrosive splash and spray zone of offshore structures to provide protection. In particular, 90-10 copper-nickel (C70600), 70-30 copper-nickel (C71500) and 70-30 nickel-copper (Alloy 400) have been successfully used to improve the corrosion resistance of steel pilings[C - 1,2,3,4]. The latter material, 70-30 nickel-copper (Alloy 400) has also been advantageously utilized in the spray and splash zone of hot risers.

Initially there were concerns that the steel below the tidal zone might become anodic and thus experience accelerated corrosive attack when the spray and splash zone is clad with a more noble alloy such as the copper-nickels and 70-30 nickel-copper (Alloy 400). However, in practice, it has been found that the steel below the tidal zone is cathodic relative to these more noble sheathing alloys[C - 5,6] because it becomes polarized to the potential of the adjacent submerged steel. Therefore, the submerged steel structure on sheathed pilings corrodes at a lower rate than the submerged steel on a bare or unsheathed steel piling.

The copper-nickel alloys have not only good seawater corrosion performance, but also resistance to biofouling[C - 7,8,9,10]. This biofouling resistance is intrinsic in 70-30 copper-nickel, but is even greater in 90-10 copper-nickel by virtue of its higher copper content. It is generally accepted that 90-10 copper nickel is the material of choice for sheathing pilings because it offers the best combination of corrosion resistance, biofouling resistance and cost relative to either 70-30 copper-nickel or 70-30 nickel-copper (Alloy 400), as confirmed by an Exxon economic assessment[C - 11]. Since the 90-10 copper-nickel shows superior biofouling resistance, the loads associated with the waves, currents and tides are lower since the structure presents a smaller cross-section to these forces. Lower loading, as well as a reduction in corrosion allowance,

translate into savings related to the reduced weight of the structure. The reduction in weight can be realized not only by sheathing steel but also concrete structures. A British Gas economic assessment related to sheathing in the Morecambe Field[C-12] in the UK is one example of the quantification of these savings, and is shown in Table 1. Shell measured savings related to using 90-10 copper-nickel over an insulating elastomer applied to steel pilings in California;[C-13] this is presented in Table 2. They chose to insulate the alloy sheathing because it provides greater biofouling resistance than when the sheathing is applied directly to the bare steel[C-9,10].

Hot risers, clad with 70-30 nickel-copper (Alloy 400), have been reported to be first used in the Arabian Gulf in the late 1950s[C-14]. Another paper[15] in these proceedings expanded upon the successful utilization of 70-30 nickel-copper (Alloy 400) for hot risers in the Middle East, as well as the North Sea and salty Lake Maracaibo in Venezuela.

Some limited field experience in sheathing steel pilings with 18-8 chromium-nickel (Type 304) stainless steel[C-13,16,17] have also been gained. Corrosion of the bare steel below the tidal zone can be controlled as long as sacrificial anodes are provided. However, 18-8 chromium-nickel (Type 304) stainless steel is not used on hot riser because of concerns related to stress corrosion cracking, to which it is susceptible above ambient temperatures. Thick zinc cladding has been specified by Shell Oil for the hydraulic control lines of wellheads positioned directly on the seabed. The feasibility of using arc-sprayed pure copper and 90-10 copper-nickel has been demonstrated[C-18]. Furthermore, thermal spray aluminum is routinely used on steel pilings to reduce the corrosive action of seawater.

Adhesively-backed thin foil of 90-10 copper-nickel, known by the trade name of MITCHELL MARINER 706, has been extensively used for sheathing pleasure boats[C-19] including hulls made of wood, glass reinforced plastic (GRP), and steel. Additionally, this foil has been applied to two small ferries in New Zealand[C-15]. This approach should be equally useful on steel pilings.

An undersea pipeline identification system known as SEAMARK, which is biofouling resistant and thus readable in seawater by divers has been commercialized. It consists of 90-10 copper-nickel (C70600) mesh embedded in a resin[C-20]. This resin must be abraded before placement in seawater in order to expose the copper-nickel, which resists biofouling. In 1993 more than 2000 of these types of pipeline markers were sold for application in the North Sea[C-15]. In summary, the installation of metallic sheathing, with any one of a variety of alloys can improve the corrosion resistance and thus extend the life of steel pilings. Hot risers can also be sheathed with alloys and 70-30 nickel-copper (Alloy 400) has been widely used in this application with success. In regard to the splash and spray zone of pilings, sheathing with the copper-nickel alloys provide the additional benefit of biofouling resistance, which translates into savings by reducing structure size and maintenance. The optimum combination of corrosion resistance, biofuling resistance and savings can be achieved by utilizing 90-10 copper-nickel to sheath steel pilings.

7

TABLE 1

ANALYSIS OF SYSTEM COSTS FOR SEVERAL COATINGS OR SHEATHINGS FOR SPLASH ZONE PROTECTION
System Costs, Million Pounds Sterling

	Protective Coating/Sheathing			
	Paint	Neoprene	Alloy 400	90-10 Cu-Ni
Initial Cost - Extra Steel	2.3	2.3	-	-
Protective Material & Labor	0.1	0.3	2.2	0.95
Maintenance Cost	2.4[1]	unknown[2]	0.15[3]	0.15[3]
Extra Weight (tonnes)	660	660	180	180

[1] Repainting 8 years after installation and every 5 years thereafter

[2] No long-time experience; no large scale repairs assumed in less than 18 years

[3] Minimum maintenance, confined mainly to accident repair

TABLE 2

ESTIMATES OF COST SAVINGS FOR OFFSHORE INSTALLATIONS BY USING A 90-10 COPPER-NICKEL INSULATED SHEATHING SYSTEM

Conductors - 55 tons x $1000/ton	=	$ 55,000
Paint - 10,600 ft.^{2} x $3/ft^2	=	32,000
Anodes - $1250 each x 4	=	5,000
Structural Nodes - 114 tons x $2500/ton	=	285,000
Total	=	$377,000
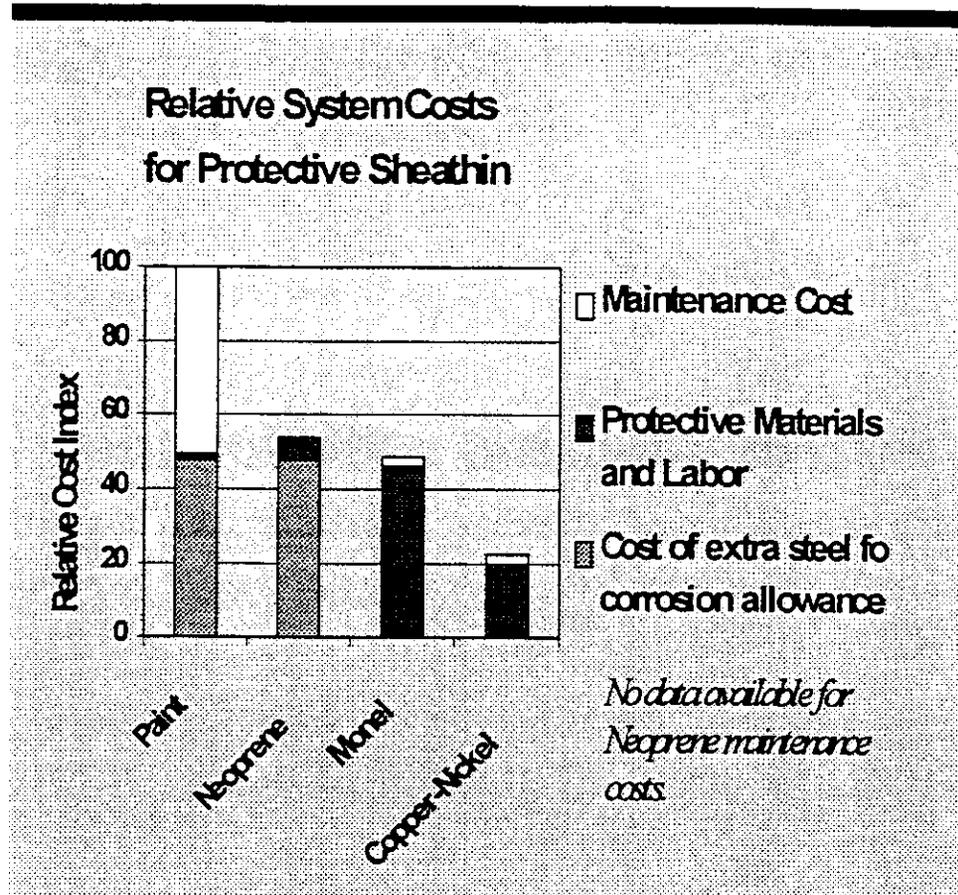
Figure 1 - Relative System Costs for Protective Sheathing

Research and development in High Velocity Thermal Spraying processes at the GKSS Research Center in Geesthacht, Germany using coatings of different high density materials have demonstrated acceptable roughness and good bond to the substrate for corrosion protection in the splash zone and other shallow water applications. The density is an important factor with thermal spray applications to prevent water or moisture entering the coating and damaging the bond to the base material. The limitations are the length of the supply hoses and the related pressure loss to the gas supply. This technology is presently still under development but one to watch as it evolves [ref. C - 22].

6.0 MATERIALS OF CONSTRUCTION

With structural materials available today or in the immediate future, it is difficult to beat common steel for cost, strength, and a proven track record. In many niche markets, however, non-ferrous materials such as titanium and composites, are being used as light-weight, corrosion resistant replacements for steel. As the technology of fabricating and joining these materials advances, and as prices drop, they may be used even for the structural components of offshore facilities.

9

The strength of new structural material in the Gulf of Mexico range from 50 to 60 ksi in joint cans with good through thickness and toughness. All remaining structural materials are generally36 ksi. High strength steels exceeding 60 ksi are generally not used except in special applications and Jack Up Structures where components reach 110 ksi. The offshore petroleum industry is currently focusing on the use of advanced materials for risers and stress joints in deepwater developments. Will this be a spring-board for the development of larger diameter tubular members that can be used to build fixed structures?

Certain alloys of titanium and various fiber reinforced polymer (FRP) materials are being considered for a number of offshore applications. Their low modulus, excellent fatigue properties and corrosion resistance are reasons for their current use as tapered stress joints (27 are in service or ordered at this writing). Their low weight and high specific strength (yield strength / density) can reduce the tension loads required for drilling and production risers. However, with the exception of one drilling riser, none of these have been placed in service to date. As the cost of these materials decreases and as more experience with them increases, there will be certain niche applications where they will gain wide acceptance.

6.1   High Strength Steels and Associated Cathodic Protection Systems Used In The North Sea.

Fixed Offshore Installations in the UK sector of the North Sea are predominantly constructed from steels with yield strengths of 355 MPa. The higher strength steels with nominal yields of 450 MPa are increasingly being used for brace members and leg sections away from the fatigue sensitive node joint areas. The design of the Cathodic Protection system is, in the main, conventional for these installations.

Use of high strength steels with yields greater then 500 MPa has generally been for the leg chord and rack sections of jack-up type mobile drilling installations. More recently jack-up type fixed installations have been used in place of conventional jackets. In the UK sector there are two such installations in operation with a third under construction. During the late 80s cracking in a number of drilling rigs registered for operation in the UK sector of the North Sea was found in the lower leg sections and spud cans. The subsequent research identified the cause as hydrogen assisted cracking (HAC).

The guidance resulting from this research and included in the July 1993 update of The HSE Offshore Installations: Guidance on Design, construction and certification, 4th edition, warned that commonly used CP systems are likely to give excessive negative voltages which may render high strength steels susceptible to hydrogen embrittlement and recommended implementation of alternative CP systems offering controlled voltages with a predetermined limit. Additional recommendations included; evaluation of the susceptibility of high strength steels to hydrogen embrittlement at appropriate cathodic potential levels and expected environment (anaerobic conditions, presence of H2S), control of assembly methods to restrict the residual stresses and hardness levels in weld heat affected zones to levels shown to be acceptable by tests and implementation of Quality Assurance programmes to ensure that the specification requirements

are met during all phases of an installation's life including regular surveys of CP voltages in the vulnerable areas.

All three fixed installations mentioned above have sought to reduce the potential hydrogen embrittlement problem by employing CP systems designed specially for the particular design and location of the installation. The first of these installations is an old drilling rig that has been converted to an accommodation platform stationed next to a newer production jacket platform. Slow strain tests indicated that the high strength Jack-up leg steel is susceptible to hydrogen embrittlement and hence a Schottky diode based CP system has been installed to limit the potential to -850mV. Although connected by a bridge, cables and pipe work, the two installations are electrically isolated. Failure of cable gland and pipe insulation would allow stray leakage current from the adjacent structure that has normal CP potential more negative then -950mV to drive the jack-up CP potential more negative then is safe for the leg steel. To mitigate against such excursions an impressed current system has been installed. Detection of the drift in the potential by reference electrodes mounted on the legs trigger the system to inject current to restore the potential to within the safe operating envelope.

The other two more modern jack-ups have been designed specifically for the North Sea as fixed production installations and hence more detailed consideration has been given to the steel metallurgy and welding procedures, stress levels and the design of the cathodic protection system. On both installations, steels with nominal yield strengths of 690MPa have been restricted to above water leg sections and the rack. Below water, 500MPa nominal yield steel for chord members and 400 MPa nominal yield steel for brace members have been used. The latter two steels are considerably less sensitive to hydrogen embrittlement. The CP system on one of the installations has been based on the use of commercial sacrificial anodes in conjunction with potential limiting diodes (Schottky barrier diodes) to achieve a potential in the range between - 770mV and -830mV. Selected areas of the legs are monitored using permanently installed dual siver/silver chloride and zinc/seawater reference electrodes. Annual survey of potentials is also undertaken using ROVs. Bracelet type anodes have been used because they are easier and cheaper to install. For the second installation a conventional CP system is proposed based on the results of an extensive test programme demonstrating the reduced sensitivity of the proposed steels to hydrogen embrittlement. Additionally the interaction of the jack-up CP system with the adjacent well head jacket and pipeline systems could be difficult to control or prevent.

The research information on modern high strength steels has indicated that provided the conditions are properly controlled these materials can be used safely. The use of high strength steels in fixed structures is novel and therefore it is important to monitor the performance of these materials to ensure safe operation.

7.0   STRUCTURAL DESIGN DEMANDS

7.1   Reduced Conservatism in Design

Structural design of offshore facilities is very conservative. While conservative design may be considered by some to be wasteful and costly, to others conservative design is cheap insurance. The later has proved to have some merit considering the number of structures that have exceeded

their design life and are still producing. One way to reduce the cost of these facilities is to reduce the degree of conservatism while allowing room for future upgrades and unforeseen structural demands. As this trend develops, it will be more and more critical to control corrosion reliably. Integrated analysis of minimum designs with the risks of reduced strength due to long term degradation of the materials will require risk-based analysis of the corrosion control system. For example, with conventional CP design, what is the risk that a certain size pit will develop in a critical node within the design life of the structure? If the number of anodes is increased by 25%, how does the risk change?

As field development profit margins have decreased, there have been increased pressures on designers of offshore platforms to reduce the 'conservatisms' in the structures. The reductions in conservatisms have been translated into reductions in initial costs and the increased popularity of 'minimum' structures (Craig, 1995).

The effects of corrosion on minimum and conventional steel, template-type platforms has been studied (Bea, Craig, Miller, 1997; Aviguetero, Bea, 1998). Results from one of these studies is summarized in Figure 1 (general corrosion) and Figure 2.

Even though both of the structures are designed to have the same lateral loading capacity, as corrosion develops in the critical structural elements of the structures, there is a dramatic difference in the abilities of the structures to tolerate the corrosion damage. The conventional 'robust' structure design is able to tolerate much more corrosion damage than the comparable minimum platform. The combination of redundancy, ductility, and excess loading capacity in the conventional structure translates to greater initial costs, but, greater tolerance to corrosion damage and defects.

These results clearly show that if minimum structures are to have the same capacity through life as that of a comparable conventional structure, then the attention to corrosion protection must be even greater than for conventional structures.
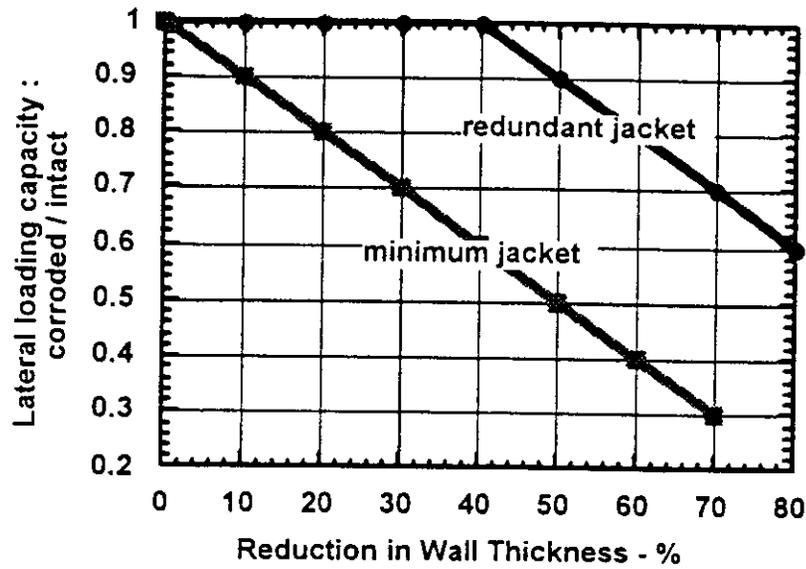
Figure 1: Effect of brace general corrosion on structure lateral loading capacity
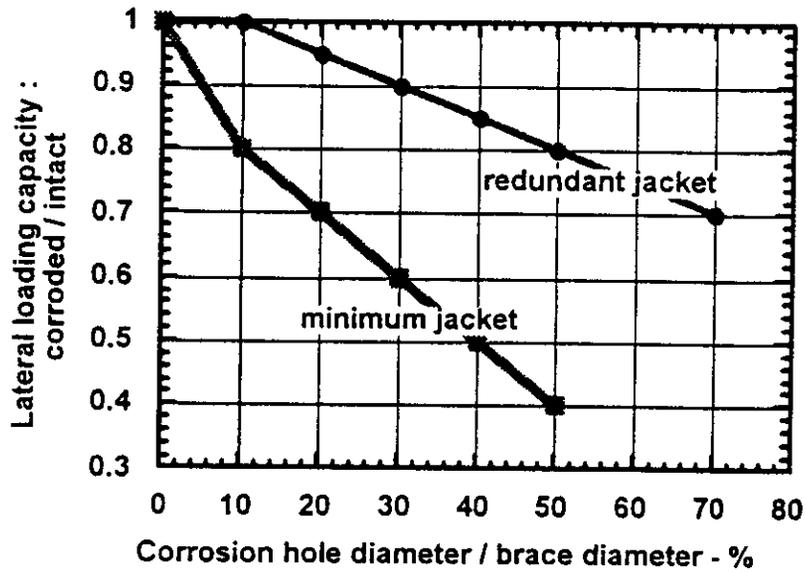
Figure 2: Effect of brace local corrosion on structure lateral loading capacity

7.2   Streamlined Projects

One of the major factors affecting the ultimate profitability of a petroleum development is the development time.   Oil companies are under enormous pressure to reduce the time from discovery to first production.   Anything that slows the process is likely to be overlooked, or addressed after the fact. On the other hand, the only way to have a major impact on the capital cost of new developments is to incorporate new technology. To effectively use technology, it is critical that companies include technologists in the early planning for a development, to apply new analysis methods, new materials of construction, and new corrosion control approaches. Unfortunately, application of new technology often takes a back seat, as the design teams rely

13

solely on proven internal or external design standards. For example, the corrosion engineer asking for a few days in the fabrication yard to touch up coating along weld lines may be out of luck, so it is prudent not to build a high coating efficiency into a CP design. In fact, in many cases the corrosion engineer is being asked to review committed plans, for which any changes will be expensive.

7.3 Design/Build Packages

In the quest for speed and efficiency, oil companies are looking to design/build engineering firms or consortia for complete packages from design to installation. These companies are unlikely to incorporate new technology into their designs, as they normally do not retain dedicated corrosion control expertise on board. In these cases, not only is the corrosion engineer consulted late in the game, but he must now convince two companies of the necessity of any design changes.

In general CP of structure is relied upon to protect conductor risers. The splash zone areas are of the greatest concern. Adding sleeves from below the water level to above the water level are cost effective in preventing corrosion at the splash zone elevations. For instance, a thirty foot long, large diameter clamshell made of a relatively thin sheet of titanium could be fastened around and grouted to an existing and corroded cassion on an offshore structure. This would be a long term, cost effective solution to an environmental and safety hazard.

As previously stated, in many cases fixed structures are exceeding their design life. If new structures are going to follow this same trend it is recommended that anode design be modified to take into account future retrofitting by use of remote operated vehicles vs divers should the structure go beyond its design life.

8.0 QUALITY ASSURANCE

While quality has improved significantly since the introduction of ISO 9000 and other quality initiatives, costly quality related failures are still prevalent in many CP projects. Quality assurance (QA) is the planning, organizing, implementing and controlling of work activities required to ensure a job meets the specified requirements. Design specifications for corrosion protection of fixed offshore structures should describe the specific QA functions to be performed. The design specification for each type of CP (e.g. sacrificial anodes, organic or metallic coatings, materials, etc.) for new or retrofitting of existing structures should include:

8.1 CP design basis

    a.   CP design information
    b.   Desired CP life
    c.   Performance requirements
    d.   Approved for Construction or As-built drawing
    e.   CP analysis data

8.2 Fabrication / Installation Design Requirements

    a.   End results required

b.   Options available
c.   Standards & requirements for workmanship
d.   Consequences of deviation
e.   Materials
f.   Processes
g.   Resource requirements (e.g. services, equipment, etc.)
h.   Documentation & quality record requirements
i.   Procedures

QA activities for CP require the coordination and interaction of various parties responsible for managing, performing and verifying the work. To ensure good engineering practice is followed by all responsible concerns, more emphasis on quality assurance during procurement, fabrication and installation is needed to include:

8.3   QA During Procurement

a.   Conduct Purchase order reviews to ensure quality of materials, components and contractors essential to CP are procured in accordance with specified requirements.

b.   Ensure proper transfer of appropriate technical information to those persons who will use the information to purchase materials, components and contractors for fabrication and installation of CP systems.

c.   If an engineering specification has not been developed, the quality needs should be verified with engineering or responsible personnel to ensure the requirements are understood and met.

d.   Suppliers should be qualified and pre-approved

e.   Records and certification documents related to materials / components should be requested on the purchase order or contract specification.

f.   Purchase order documents, certification documents, labeling, markings and other records should be reviewed on existing materials / components and checked upon receipt to ensure they meet the specified requirements before use.

g.   No material or component should be used if verification of specified requirements cannot be obtained.

h.   Personnel responsible for purchasing and receiving should be trained in purchasing requirements for CP.

i.   All documentation and QA records should be maintained for traceability of CP materials and components.

j.   Ensure that receipt of purchased CP materials and components are in accordance with the specified requirements before fabrication or installation.

k.   The projects QA program should include provision for identifying, documenting, segregating, storing, disposition of nonconforming items, and material deficiencies.

8.4   QA During Fabrication and Installation

a. QA information management and tracking begins with the CP project specification(s).

b. A QA plan should be established to ensure all required CP project activities are accounted for, responsibilities are communicated and records completed verifying completion of the work performed and archive for future reference.

c. Pre-fabrication / installation meetings are recommended to be held with the contractors / vendors that have been enlisted to perform the work to review CP project requirements.

d. All parties should be aware of the inspection requirements, the inspection plan to include hold points, requirements for resolving non-conformities and / or project variances identified during fabrication or installation.

e. Inspection and test report forms or reports should be developed for the CP project and used to record inspection and testing activities and personnel who perform them.

f. Any inspection and test report that records a non-conformity should identify the follow-up inspection report or other document that represents the action taken to resolve the nonconformity.

g. Requests for variances should be documented.

h. All variances should be analyzed by the responsible representative for their impact on the CP project specification requirements and either rejected, approved with clarification or approved as submitted accordingly.

i. CP fabrication and or installation should not continue until the variance has been approved and clarifications or additional instructions communicated.

j. Inspection records related to QA of CP fabrication and or installation should be maintained by the issuing department to facilitate retrievability of the documents.

k. Inspection records as a minimum should identify: date of inspection; project I.D. and CP applied; description of the inspection performed results of inspection performed; and the name of the person who performed the inspection.

All CP systems for fixed offshore structures have a lifecycle. Quality assurance of purchasing and receiving are equally as important as quality assurance during fabrication, installation and in-service maintenance to ensure optimal CP performance. Information tracking is essential to verify compliance to specified requirements, maintain the desired CP performance over the course of its lifecycle and update of CP systems as new technologies are introduced and or design life is exceeded.

9.0 MONITORING, INSPECTION AND TESTING

The state-of-the-art in monitoring for offshore structures is the annual drop cell survey combined with visual inspection on a 5-year schedule. For the most part, this has been adequate to detect failing or inadequate CP systems, and to find rare cases of structural damage. However, the frequency and accuracy of data collection are inadequate to draw firm conclusions about why changes in the polarization state of a structure are occurring, either during the hoped-for development of initial polarization or at the end of anode life where polarization is being lost. Generally, if problems are seen in the polarization state, collection of further data is needed before the cause can be identified. For larger structures in somewhat deep water, collecting this

additional data can be a major undertaking, and may take a few years to accomplish. The approval process, budgeting, and planning may also take a number of years to accomplish.

The annual inspection or Level I, (API RP 2A), inspection generally consists of a topside inspection from the waterline upward of coating and structural elements and a drop cell Cathodic Potential Survey of the structure and risers.

The purpose of the drop cell CP survey is to assess the adequacy of the cathodic protection system for the structure and risers. The equipment recommended is the Silver/Silver Chloride (Ag/AgCl) reference electrodes (proximity type). Generally the reference electrode is lowered as close as possible to each of the legs and risers and readings are obtained at the surface and in 10' increments. The annual drop cell survey does show if the CP system is working or failing at the time of inspection, but no information of the amount of material remaining on the sacrificial anodes can be obtained. The drop cell survey is only a proximity reading and with currents or obstructions the actual location of probe is unknown.

The 5 year visual inspection may entail a Level II or III, (API RP 2A), inspection by divers and or ROV's. The Level II inspection generally consists of, but not limited to, a Visual Inspection from top of jacket to mudline determining the presence of excessive corrosion, presence of debris and amount of marine growth. To assess the adequacy of the cathodic protection system of the major structural components from the splashzone to the mudline the Cathodic Potential Survey using the Silver/Silver Chloride (Ag/AgCl) reference electrodes (proximity type) is used as stated above. Components to be surveyed may include, but not be limited to, Legs, Conductors, J-Tubes, Risers, Members and Anodes. There is higher accuracy of the data collected when using divers or ROV's in comparison to the drop cell method, due to the fact that the actual location of the probe is known. Other surveys include: Anode Survey, Debris Survey, Bottom Survey, Marine Growth Survey, Riser/Pipeline/J-Tube and Process Equipment Survey, Conductor Survey and Flooded Member Detection. The Level III inspection generally includes items of a Level II inspection and a Selected Node/Weld Survey by divers.

The Anode Survey is to assess the depletion rates and useful life expectancy of the platform's sacrificial anodes as well as verify the type and the quantity of these anodes. The typical information gathered on specified anodes are: the location, estimated depletion of anode, CP reading on the anode, CP reading on the component the anode is mounted to, 180 around component from the anode, attachment status, anode type, electrical attachment type, extent and average size of pitting in anode, length of anode, circumference at each end and the middle of the anode and the circumference of the core pipe of the anode.

Debris survey is to generate a detailed description of any debris found in contact with the platform and record any damage caused by the debris as well as give an indication of any additional loading on the structure's cathodic protection system.

Selected Node/Weld Survey is to provide a detailed visual inspection of selected welded joints to quantify defects, anomalies and corrosion, which may not be detected during the general visual inspection of the jacket. It has also been seen once nodes are cleaned to bare steel removing marine growth, calcareous deposits and black oxides, if present, a 30 mV to 50 mV drop, (more

positive), in the CP readings compared to readings taken prior to cleaning. The Selected Node/Weld Survey has also revealed isolated cases of corrosion even when the CP readings are more negative then -800 mV.

Although the answer seems clear at first glance, it is clouded by the drop-off in anode efficiency as anode current density is reduced, as discussed above. The state-of-the-art now recognizes that properties of galvanic anodes, aluminum in particular, are dependent synergistically upon a) alloy composition and microstructure (a-j), b) electrolyte properties including composition, temperature and velocity (j,k-o), c) current density (j,m-q) and d) exposure time (f-h,l,n,q,r). Also, there is presently no short-term or accelerated test procedure that can predict long-term service performance. Despite this, the results of accelerated tests are often used to project such performance, as noted above. A major contributor to this lack of correlation between short- and long-term test results may be that an acidic condition develops with time beneath the corrosion products upon anodes (l) but accelerated testing is performed in near-neutral solutions. This probably contributes to the recent finding that current capacity over the long-term is less than what has been incorporated into the design protocols of recommended practices (s). Additional studies are needed to address this and to resolve what appears to be a non-conservative aspect of present cp design practices.

The economics of a particular field development are always based on a life expectancy for the field and facilities. In the past, a facilities design life of 20 years has been common, although today new developments may have 30 or more years design life. (A longer design life generally gives a project a higher net present value, since the capital investment in these projects is quite high and it takes several years to achieve a positive net cash flow position. On the other hand, all other factors being equal, a production company would prefer to develop a project which meets its return-on-investment criteria based on a 20 year life rather than one with a 30 year life – net income generated earlier in the life cycle can then be used to fund other projects.) In practice, the field life is almost always greater than the facilities design life and so equipment must be kept in service either by repair, replacement, or fitness-for-service review.

As noted above, the principle of rapid polarization is an integral part of present cp design practice. By this, a sufficiently high current density is applied initially to polarize the structure to near −1.00 v (Ag/AgCl) such that a particularly protective calcareous deposit forms and current density is lower than if potential were more positive (-0.85 v, for example). The recently proposed slope parameter approach to affecting rapid polarization represents a powerful design tool for accomplishing this; however, the method is yet to be incorporated into standard recommended practices.

Figure – 9.1 schematically illustrates the long-term potential-current density curve for steel in temperate sea water in perspective to four different design approaches, each of which is characterized by a value for the slope parameter, S, for which

$$S = \frac{\Delta \phi}{i} = \frac{R_a \cdot A_c}{N},$$

18

where

> $\Delta\phi$ is the anode-cathode potential difference,
> i is cathode current density
> R_a is resistance of an individual anode,
> A_c is cathode surface area, and
> N is the number of anodes.

Thus, design according to S_1 results in underprotection, while with S_2 protection is achieved but at an unnecessarily high current density. For slope parameter values in the range S_3-S_4, however, protection is achieved with minimum current density.

Figure – 9.1

CURRENT DENSITY
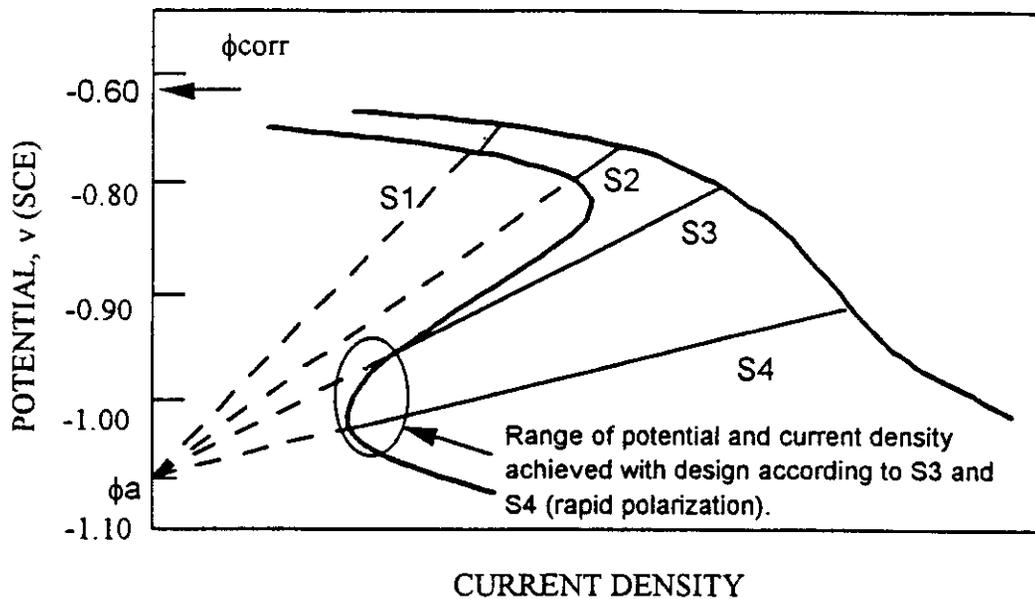
Either of two factors, storm activity or loss of anode function (or a combination of these), can compromise cathodic protection and lead to corrosion. The former (storm activity) causes enhanced oxygen availability, either in conjunction with greater water movements or physical damage to the calcareous deposit film (or both), which cause depolarization. In this case, the depolarization is along the slope parameter line that prevails at a particular time, as defined by R_a or, alternatively, $\Box\Box$ (see Equation -). A critical question is the extent to which repolarization will occur once the storm subsides. This will be determined by the value for S, as affected by R_a or by the anode dimensions (the extent to which the anode has wasted). Loss of anode function (factor two above, on the other hand, can result from either anode passivation or depletion. The former (passivation) typically results in a positive shift in $\Box_a$ and a corresponding increase in potential for the cathode to more positive values. This is accompanied by an increase in slope of the anode polarization curve (not to be confused with the slope parameter, S) such that the ability of the anode to affect polarization is diminished. Alternatively, depletion results in a reduction in anode dimensions and a corresponding increase in R_a and, hence, S. However, as long as

polarization is such that $\square_c \leq$ -0.80v (AgAgCl), the calcareous deposits should remain in tact and structure current demand should be low. Once the structure begins to corrode though and the calcareous deposits become undermined by corrosion products and spalls away, current demand should increase. This could result in a requirement that retrofit cp designs be such that current densities be provided that are comparable with those required for the initial rapid polarization. Consequently, an economic incentive exists to ensure that retrofit intervention transpires prior to significant depolarization; that is, prior to potential becoming positive to –0.80 v. Figure – 9.2 illustrates these two depolarization scenarios schematically in perspective to a steady-state cathodic polarization curve that has been determined to apply for near-surface semi-tropical waters.

CURRENT DENSITY
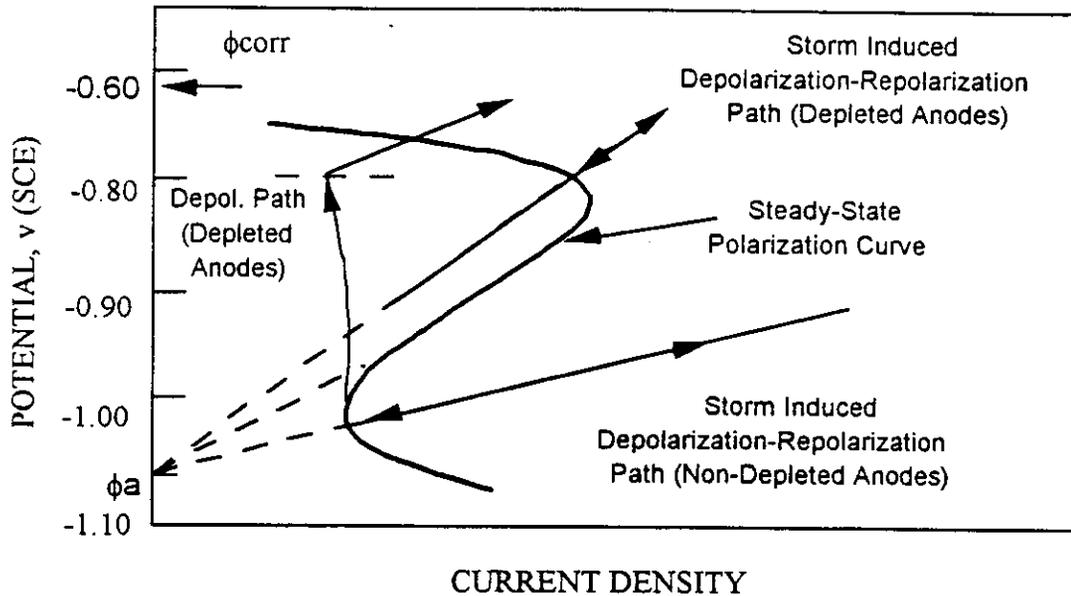
Figure – 9.2

Visual inspection is the primary technique for monitoring the condition of the corrosion-prevention system in the splash zone and above the water. In particular, visual inspection can detect deterioration in the organic coatings, cladding or sheathing normally used to protect the steel members in these portions of the structure. It is not necessarily easy, however, to tell how much steel has been lost in locations where the protection has been damaged and some corrosion is obvious. In addition, these portions of the structure are particularly susceptible to mechanical damage resulting from collision with boats and barges, or objects dropped from the deck. This mechanical damage can cause holes, or splits in the tubular members, as well as dents and bends. In addition to external damage of the corrosion-protection system, such holes or splits can provide a supply of water and oxygen to the internal surface of a member, thereby creating a corrosive environment in a location which cannot be monitored visually. Thus, even though the holes or cracks may be detected by visual inspection, it may be difficult to assess the corrosion damage to the structure.

There is not standard technique for measuring the damage done by visible corrosion, or of monitoring internal corrosion of a structural member. Ultrasonic (UT) waves, though, provide

one potential method. Relatively inexpensive and portable devices UT devices have been developed specifically for the purpose of making one-sided measurements of thickness, and these devices could potentially be useful in monitoring the remaining wall thickness of in-situ tubular structural members with either internal or external corrosion. Before this becomes practical, though, it will be necessary to know more about the corrosion which develops in these portions of the structure. In particular, information is needed about the statistical variation of corrosion damage over the length and circumference of a member, and about the distance over which this corrosion is highly correlated. This information will determine the spacing necessary for UT measurements, and the locations on the member which are most likely to provide useful information. Without this information it is not feasible to design a monitoring program which is both effective and efficient. Current research projects at Lehigh University and Texas A&M University should provide at least some of the missing answers.

More sophisticated permanently installed monitoring systems, such as the Polatrak line of instrumentation from InterResources, Inc. are available which can measure not only structure potential, but also the cathodic current density and the current output of individual anodes. It is possible that regulating agencies will accept these readings in lieu of yearly drop cell surveys. The Minerals Management Service recognizes Best Available and Safest Technologies (BAST) (ref. F – 10) when considering approval of new technologies. These systems currently incorporate both zinc (for long term reliability) and silver/silver chloride reference electrodes (for accuracy). The silver/silver chloride reference electrodes are usually short-lived. The monitoring systems generate small voltage signals which are easily measured by the structures process monitoring and control data system. Incorporation of cathodic protection monitoring into the normal control and data collection systems has the advantages that the data acquisition equipment cost becomes negligible, and the process for archiving and displaying data is no longer the responsibility of the corrosion engineer.

These monitoring systems are not generally part of the design specifications of the major oil companies, nor is their installation routine in most fabrication yards. Monitoring technology is advancing to wireless systems, etc. and cost effectiveness / benefit to permanent monitoring vs drop cell tests.

11.0   CONTROLLING DEFICIENCIES

Many failures in CP systems, both in new construction and in the ongoing maintenance of existing CP systems can be avoided by providing a means to assure that deficiencies are identified, and resolved in a controlled and timely manner. Defects in CP systems can be avoided by incorporating visual and other monitoring methods throughout the life cycle of the CP system. Inspection and test objectives should be determined prior to selecting an inspection method(s). Following the selection of test method(s) the inspection and test requirements (including acceptance / rejection criteria) should be established as well as inspection / testing feasibility. Inspection and test procedures should be established for each inspection method for consistency and uniformity. Once inspections are carried out problem areas should be analyzed to determine the correct course of action. The deleterious effects, steps and feasibility of repairs if required should be recorded. All inspections and tests should also be recorded in accordance with applicable requirements.

CP modification and or repairs require careful analysis and planning prior to implementation. There are many opportunities during the lifecycle of a CP system to improve CP integrity. The proper identification and control of deficiencies form the baseline for CP modification and or repairs.

12.0 MAINTENANCE AND REPAIR

The timing and manner of anode retrofit can have significant impact on maintenance costs, particularly as water depth increases (e.g. where the initial installation of anode at the fabrication yard may be only $40 thousand dollars retrofits of the same anodes using divers, saturation equipment, vessels, etc may exceed $1 million dollars). A Joint Industry Project at Florida Atlantic University is currently studying the timing issue – is there any benefit to retrofitting before a structure starts to lose polarization, or is it acceptable to reach a relatively unprotected potential before adding anodes? The project also addresses the design criteria for a retrofit. As current demand for a well-polarized structure is less than for a new installation, is it possible to use less anode material to achieve a similar design life?

13.0 BIOFOULING EFFECTS

Biological activity in sea water is divided in two major groups: macrofouling and microfouling. Macrofouling as well as microfouling can exhibit a significant impact on environmental chemistry and also on the corrosion behavior of various structural materials. Cathodic protection is used to control the corrosion of offshore structures but at the same time it may also enhance the fouling load on the structures. The creation of interfacial alkalinity by cathodic protection favors the attachment of organisms.

When a metal or other surface is first immersed in sea water, a biological slime tends to develop within a matter of hours (ref. G – 1). Subsequently, embryonic sessile organisms became firmly attached. Once attached, they rapidly transform to the mature form. However, biological growth (macrofouling) should not be a problem in deep waters since marine growth requires sunlight that is not available at depths of 1000 feet or greater.

Analysis of data reported for locations in the N.E. Pacific and N. W. Atlantic assumed that pH variations with depth are controlled by biological factors (ref. G – 2). The photosynthesis reaction consumes CO_2 and produces organic carbohydrates and oxygen. This process is limited to the near surface. Additionally, CO_2 consumption is more likely during daylight hours. The daily shift in pH is in the range of 8.0 to 8.2.

As living matter dies and decays, it tends to accumulate and so in deeper waters the reverse process takes place. This time oxygen is consumed and CO_2 is produced thereby promoting a tendency for pH to be lower in deep waters than near the surface. For open sea water pH covers a range from 8.4 to 7.4. Environmental data from off West Africa show a very low oxygen content (ref. G – 3). It is tentatively suggested that water contains biomatter which is degrading. This process utilizes oxygen and that is what observed.

Among other environmental factors like temperature, oxygen availability and velocity, pH is a major factor in calcareous scale deposition. At great depths, it will contribute to a less tendency for protective carbonate type scales to form and as was shown above this is an indirect result of biological activity.

Differences in the dissolution rate behavior of calcium carbonates for different ocean areas is considered to be related to the inhibiting effect of phosphates or certain organic acids. The growth rate of both calcite and aragonite, which are major components of calcareous deposits, is inhibited by the presence of organic matter (ref. G – 3). Some authors have studied the effect of various organic constituents on the precipitation rate of aragonite and found that organic matter had a rate retarding effect on the precipitation of aragonite.

Microbiological activity has been demonstrated on cathodic protected surfaces[4]. Cathodic potentials to -1.074 Volts have not prevent biofilm formation. Most investigators have evaluated the interrelationships of calcareous deposits and bacteria with respect to sulfate reducing bacteria (SRB). SRB predominate in anaerobic marine biofilms because of the presence of sulfate in sea water and the ability of some SRB to use hydrogen produced by acetogenic bacteria, allowing them to outcompete other species.

SRB within biofilms can reduce sulfate to sulfide that reacts with the metal surface to form corrosion products. In many cases a protection potential of -1.024 Volts is necessary for carbon steel steel in order to achieve an adequate protection from corrosion caused from activity of SRB. The potential applied is not to prevent growth of SRB, but is based on a theoretical level which will allow passivity of steel in a sulfide rich environment produced by SRB. The main consequence of a biofilm formation on protected surfaces appears to be an increase in the current density necessary to polarize the metal to the protection potential.

Macrofouling and specifically barnacle fouling (ref. G – 5) has been shown to increase the anode resistance of aluminum anodes which reduces the maximum current output to below that calculated from anode resistance formulae. Working anodes are less affected than non-working anodes. This is because anodes operating at low or zero current densities will allow total cover by marine growth to occur. Conversely, at high current densities fouling will be totally prevented due to the continuous breakdown of the anode surface.

The implications of these findings to operational procedures are important in situations where there maybe an increase in current demand from anodes operating at zero or low current densities. It has been shown that anodes 100 percent covered by barnacles will reactivate but it will be at a level bellow that calculated from anode resistance formulae.

Removal of fouling by normal cleaning methods is costly and time consuming. Commercially available systems for controlling biofouling are copper based. In that process, copper is dissolved and the toxic copper ions generated are utilized for controlling biofouling. In situ chlorine generation using electrochemical process is an emerging and promising technique to control biofouling (ref. G – 6). Research efforts are being carried out by some organizations aimed in the evaluation of the efficiency of in situ chlorine generation for controlling biofouling of marine structures and offshore platforms.

14.0 JOINT INDUSTRY STUDY CONSIDERATIONS

The following Joint Industry Study recommendations were discussed by the working group and are submitted as areas that would benefit the offshore community:

1. Recommend a JIS on test and evaluation of new technologies for CP so that data is readily available to corrosion engineers for consideration vs taking a chance.

2. Recommend a JIS on new materials and or coatings test and evaluation, particularly in the splash zone area so that data is readily available to corrosion engineers for consideration vs taking a chance.

3. Recommend a JIS on factors that effect anode efficiency (e.g. temperature hot vs cold water, resistivity, chemistry, etc.).

4. Recommend a JIS to address a more cost effective means of retrofitting sacrificial anodes.

CONCLUSIONS

In summary some areas for consideration in improving corrosion control for fixed offshore structures include:

1. Improved correlation for sacrificial anode efficiency as a function of composition, temperature, and anode current density and long-term exposure.

2. Improved reliability of impressed current systems.

3. Improved prediction of coating breakdown with time. Lower cost shop applied coatings, and more reliable and effective field touch-up coatings.

4. In the long term, use of non-ferrous, advanced materials as structural members may eliminate corrosion control costs entirely.

5. More quantitative analysis of the risks of corrosion damage will allow reductions in the conservatism of structure designs.

6. Automated collection of CP monitoring data from permanently installed sensors would allow more detailed troubleshooting of faulty systems and might be accepted in lieu of drop cell surveys by regulating agencies.

7. What is the optimum timing of and design philosophy for retrofit of sacrificial anode systems?

8. Incorporation of the recently proposed slope parameter approach to cp design into recommended practices

9. Development of models and data for projecting cp maintenance current density

Barriers to the application of new technology include:

1. The impetus to streamline the project development cycle reduces the opportunity to deploy and prove new technology, or even to properly apply old technology.

2. In design/build contracts the corrosion engineer has even less input into the design. Technologies which have not been incorporated into industry or company standards are often ignored.

3. Application of formal fully integrated quality assurance programs and systems to control deficiencies.

REFERENCES:

A. Cathodic Protection

1. (1) Murray L. Smith, Clark P Weldon, "Impressed Current Tensioned Anode Strings for Offshore Structures", MP, Number 4, 1998, p19-23

2. Cox, G. C., U.S. Patent 2,200,469, May 14, 1940.

3. Foster, T., and Moores, V. G., "Cathodic Protection Current Demand of Various Alloys in Seawater," paper no. 295 presented at CORROSION/86, March 17-21, 1986, Houston.

4. Mollan, R. and Anderson, T. R., "Design of Cathodic Protection Systems," paper no. 286 presented at CORROSION/86, March 17-21, 1986, Houston.

5. Fischer, K. P., Sydberger, T., and Lye, R., "Field Testing of Deep Water Cathodic Protection on the Norwegian Continental Shelf," paper no. 67 presented at CORROSION/87, March 9-13, 1987, San Francisco.

6. Evans S., "Use of Initial Current Density in Cathodic Protection Design", Material Performance, Feb. 1988, Vol. 27(2), pp. 9-11.

7. Fischer, K. P. and Finnegan, J. E., "Cathodic Protection Behavior of Steel in Sea Water and the Protective Properties of the Calcareous Deposits," paper no. 582 presented at CORROSION/89, April 17-21, 1989, New Orleans.

8. Schrieber, C. F. and Reding, J., "Application Methods for Rapid Polarization of Offshore Structures," paper no. 381 presented at CORROSION/90, April 23-27, 1990, Las Vegas.

9. Wang, W., Hartt, W. H., and Chen, S., "Sacrificial Anode Cathodic Polarization of Steel in Seawater," *Corrosion*, Vol. 52, 1996, pp. 419-427.

10. W. H. Hartt, Chen, S., and Townley, D. W., "Sacrificial Anode Cathodic Polarization of Steel in Sea Water - Part II: Design and Data Analysis," Corrosion, Vol. 54, 1998, pp. 317-322.

11. Townley, D. W., "Unified Design Equation for Offshore Cathodic Protection," paper no. 97473 presented at CORROSION/97, March 9-14, 1997, New Orleans.

12. Craig, M. J. K. (1995). "Minimum Offshore Structures Cost Less, Pose Higher Risk," Oil and Gas Journal, July 176, pp 33-42, Gulf Publishing Co., Houston, TX.

13. Bea, R. G., Craig, M., Miller, T. (1997). "Life Cycle Reliability & Risk Characteristics of Minimum Structures," Proceedings Offshore Technology Conference, OTC 8361, Society of Petroleum Engineers, Richardson, TX.

14. Aviguetero, T. A., Bea, R. G. (1998). "Effects of Damage and Repairs on the Lateral Load Capacity of A Typical Template-Type Offshore Platform," Proceedings 8th International Offshore and Polar Engineering Conference, Society of Offshore and Polar Engineers, Golden, CO.

15. HSE, Offshore Installations: Guidance on Design, construction and certification, 4th edition, HSE Books Sheffield UK ISBN 0 11 412961 4.

16. Det Norske Veritas, Recommended Practice RP B401 for Cathodic Protection Design 1993, Det Morske Veritas, Oslo, 1993.

17. DNV rules for Classification of Mobile Offshore Units, part 3, Structures and Equipment, Det Norske Veritas, Oslo 1996.

18. MTD Ltd, Design and Operational Guidance on Cathodic Protection of Offshore Structures, Sub-sea Installations and Pipelines, The Marine Technology Directorate Ltd, publication 90/102, London 1990, ISBN 1 870553 04 7.

19. BS 7361. Part 1 1991, Cathodic Protection, British Standards Institute, London.

20. Draft European Standard prEN 13173, Cathodic Protection for Steel Offshore Floating Structures, European Committee for the Standardisation, Brussels and BSI, London, Jan 1998.

21. Draft European Standard prEN 12473, General Principles of Cathodic Protection in Sea Water, European Committee for the Standardisation, Brussels and BSI, London, July 1996.

22. NACE Standard RP0176-94, Corrosion Control of Fixed Offshore platforms Associated with Petroleum Production, NACE International, Houston Texas 1994; and draft discussion document NACE T-7L-16, Nov 1997.

23. NORSOK Standard, Common Requirements Cathodic Protection, M-CR-503

24. Barker J C, Data Surveys of Hydrogen Assisted Cracking in High Strength Jack-up Steels, Offshore Technology Report OTO 97 072, HSE Information Services, Sheffield UK, Feb.1998.

25. Barker J and Dixon AT, Hydrogen Assisted Cracking in Jack-ups - Myth or Reality, UCL Jack-up Conference 1997.

26. Davey V S, Hydrogen Assisted Cracking of High Strength Steels in Legs of Jack - up Rigs, chapter 13 of ' Recent developments in Jack-up Platforms' ed. Boswell L F and D'Mello C, Blackwell Scientific Publications, London 1992, ISBN 0 632 03281 2.

27. Kilgallon P, Healy J and Billingham J, the Corrosion Fatigue of High Strength Steels and Associated High Strength Weld Metals, Offshore Technology Report OTO 97 065 Nov. 1997, HSE Information Services Sheffield UK.

28. Robinson M J and Kigallon P J, 'A Review of the Effects of Sulphate Reducing Bacteria in the Marine Environment on the Corrosion Fatigue and Hydrogen Embrittlement of High Strength Steels', OMAE ' 98, Lisbon, Portugal, July 1998.

29. Bennet W T Jnr, Cadiou L and Coundreuse L, Steels for Jack-up Legs, chapter 12 of 'Recent Developments in Jack-up Platforms'; ed Boswell L F and D'Mello C, Blackwell Scientific publications, London 1992 ISBN 0 632 03281 2.

30. Abernethy k, Davey V S, Fowler C M, Jacob r; Hydrogen Cracking of Legs and Spudcans on Jack-up Drilling Rigs - A Summary of Results of an Investigation, HSE Books, Offshore Technology Report OTO 91 351, 1993. ISBN 0 717 6 0614 7.

31. Trethaway K R and Roberge P R, editors, Modelling Aqueous Corrosion - From Individual Pits to System Management, Kluwer Academic, Dordrecht Netherlands and London, 1994.

32. Batt C L, and Robinson M J, 'Optimising Cathodic Protection Requirements for High Strength Structural Steels Under Marine Biofilms', 38th Corrosion Science Symposium, Imperial College, London, September 1997.

B. Coatings Organic

1. NACE Standard RP0176-94, Standard Recommended Practice, Corrosion Control of Steel Fixed Offshore Platforms Associated with Petroleum Production, NACE International, Houston, TX (1994)

2. Metals Handbook 9th Edition, Vol. 13, Corrosion, ASM International, Metals Park, OH, pp. 398-418 (1987).

3. Guidance Notes on Marine Coating Systems, American Bureau of Shipping (1998).

4.   Douglas Dopjera, BP Corporation, Coatings Technology Paper, April, 1999

C.   Coatings Metalic

1.   E.V. Creamer, "Splash Zone Protection of Marine Structures,"
        Offshore Technology Conference, Paper No. 1274, Houston, Texas, 1970.

2.   B.B. Moreton, "Report on the Protection of Offshore Steel Structures by a Metallurgical
        Method," 9th Annual Conference Petroleum Division ASME," New York, N.Y.,
        September 1954.

3.   W.W. Kirk, "Metallic Sheathing for Protection of Steel in Seawater," Materials
        Performance, 26 9 (1987) pp 23-28.

4.   R.W. Ross, Jr. and D.B. Anderson, "Protection of Steel Piling in Marine
        Splash and Spray Zones, - The Metallic Sheathing Concept," Proceedings of the Fourth
        International Congress on Marine Corrosion and Fouling, Antibes, France, June 1976, pp
        461-473.

5.   H. Arup, "Cathodic Current Demand of Copper-Nickel Sheathed Piling," Danish
        Corrosion Centre, INCRA Project No. 371.

6.   J.A. Ellor & G.A. Gehring, Jr., "Galvanic Corrosion of Copper-Nickel Sheathed Steel
        Piling," Ocean City Research Corp., INCRA Project No. 368. March 1987.

7.   C.J. Gaffoglio, "Concepts in Corrosion and Biofouling Control Using Copper-Nickel,"
        Proceedings of the First OMAE Specialty Symposium on Offshore and Arctic Frontiers,
        New Orleans, Louisiana, Feb. 23-27, 1986.

8.   D.G. Melton, "Review of Five-Year Exposure Data for CuNi-Sheathed Steel Pilings,"
        Proceedings of the 23rd Annual Offshore Technology Conference, Houston, Texas, May
        1991, pp 221-233.

9.   S.J. Pikul and B.S. Phull, Thirteen Year Results of Long-Term Copper-Nickel Sheathed
        Piling Studies, Annual Report, ICA Project No. 358, June 1988.

10.   S.J. Pikul and B.S. Phull, Splash Zinc Corrosion of C70600 After Ten Years Exposure in
        an Oceanfront Environment, Annual Report, ICA Project No. 399, June, 1998

11.   W.R. Barger, L.D. Downer, J.E. Brown and T.R. Gaul, "Economic Evaluation - Use of
        Copper-Nickel Alloy for Sheathing of Offshore Structures," Exxon Production Research
        Company, INCRA Project No. 359, September 1984, pp 21-41

12. R. Carruthers, "The Use of 90/10 Copper-Nickel Alloy as a Splash Zone Cladding," Paper 6, Proceedings of CDA Conference on Copper-Alloys in Marine Environments, (Birmingham, England) April 1985.

13. R.F. Engel & J.P. Ray, "Bio-Shield: An Anti-fouling System for Offshore Platforms that Works!," Proceedings of Ocean Engineering and the Environment Conference, San Diego, California, United States, Vol. 1, 1985, p. 62.

14. D.J. Hopkins, "MONEL Alloy 400 Sheathing for Complete Splash Zone Protection," Offshore Europe 77,Aberdeen, September 1977.

15. D.T. Peters, H.T. Michels and C.A. Powell, "Metallic Coatings for Corrosion Control of Marine Structures," International Workshop on Corrosion Control in Marine Structures and Pipelines, February 9-11, 1999, Galveston, Texas.

16. R.M. Kain, "Performance and Fundamentals of Engineering Alloys in Seawater and the Marine Atmosphere," Presented at Innovations Marine Materials and Technologies Conference, La Spezia, Italy; October 1-3, 1992.

17. R.M. Kain, "Stainless Steel Sheathing for Splash and Spray Zone Protection of Steel Pilings, A 40-Year Case History," prepared for the Nickel Development Institute, June 8, 1998.

18. R.A. Perkins and D.L. Marsh, "Thermal-Sprayed Copper-Nickel Coatings on Steel," Final Report on INCRA Project 376, August 1990.

19. Canadian Yachting, August 1986, p. 18.

20. K.E.J. Miller, "Copper-Nickel Composites for Long-Term Anti-Fouling: A Review of Recent Applications," Proceedings of the Conference on Marine Engineering with Copper-Nickel, p. 95 (London, England: The Institute of Metals, 1988).

21. ANSI / AWS C2.20-99/C2.20-99 "Specification for Thermal Spraying Zinc Anodes on Steel Reinforced Concrete:"

22. International Workshop on Underwater Welding of Marine Structures, Dec. 7-9, 1994 "Underwater Thermal Spraying – A Viable Alternative to Conservative Corrosion Protection Systems", by Peter Szelagowski – GKSS Research Center Geesthacht, Germany

D.   Materials

1. "Critical Design Aspects of Dynamic Titanium Alloy Risers", Carl F. Baxter and Ronald W. Schutz, RMI Titanium Company, International Workshop on Advanced Materials for Marine Construction, February 4-7, 1997, New Orleans, Louisiana.

2.   "Composites for Marine Construction", Mamdouh M. Salama (Conoco), Steve Borleske (DuPont) and Jerry G. Williams (Conoco), International Workshop on Advanced Materials for Marine Construction, February 4-7, 1997, New Orleans, Louisiana.

3.   "Titanium for Marine Applications", John Mountford, Jr. and James S. Grauman, TIMET, International Workshop on Advanced Materials for Marine Construction, February 4-7, 1997, New Orleans, Louisiana.

4.   "Recent developments in titanium alloy application in the energy industry" R.W. Schutz and H.B. Watkins, RMI Titanium Company, Materials Science and Engineering A243 (1998) 305-315.

5.   "Material Requirements or Risers", F. Joseph Fischer (shell E&P), King Him Lo (Shell Oil Products) and Su-Su Wang (the University of Houston), International Workshop on Advanced Materials for Marine Construction, February 4-7, 1997, New Orleans, Louisiana.

6.   "The Coming Age of Titanium for Application to Marine and Offshore Oil and Gas Systems", James S. Grauman and John Barber (TIMET), International Workshop on Corrosion Control for Marine Structures and Pipelines, February 9-11, 1999, Galveston, Texas.

7.   Reding, J. T. and Newport, J. J., Materials Protection, Vol. 5(12), 1966, p. 15.

9.   Smith, S. N. and Goolsby, A. D., "A Consumer's Perspective of Aluminum Anode Quality Test Design," paper no. 552 presented at CORROSION/96, March 24-29, 1996, Denver.

10.   Bessone, J. S., Suarez Baldo, R. A., and DeMicheli, S. M., Corrosion, Vol. 37, 1981, p. 533.

11.   Rosasco, A. L., "A Review of the Metallurgical Aspects of Aluminum Anodes for Cathodic Protection," Report No. DTNSRCDC/SME-84-64, October, 1984.

12.   Mondoflo, L. F., Aluminum Alloys: Structure and Properties," Buttersworth, London and Boston, 1976, pp. 302 and 527.

13.   Reboul, M.C. and Delatte, M. C., Materials Performance, Vol. 19(5), 1980, p. 35.

14.   Reboul, M.C., Gimenez, P. H., and Rameau, J. J., Corrosion, Vol. 40, 1984, p. 366.

15.   Murray, J. N., Hays, R. A., Lucas, K. E., and Hogan, E. A., ," paper no. 545 presented at CORROSION/96, March 24-29, 1996, Denver.

16.   Murray, J. N., Hays, R. A., Hack, H. P., and Bieberich, E. B., "Testing of Indium Activated Aluminum Alloys for Consumable Anodes in Cathodic Protection Applications," 9th Internaval Corrosion Conference, Monterey, CA, April, 1992.

17. Hori, Y., Takao, J., and Shomon, H., Electrochemica Acta, Vol. 31, 1986, p. 555.

17. Schreiber, C. F., Cathodic Protection: Theory and Practice, Chapter 5, Eds. V. Ashworth and C. J. Booker, Ellis Horwood Limited, London. 1986.

18. Espelid, B. Schei, B., and Syderberger, T., "Characterization of Sacrificial Anode Materials Through Laboratory Testing", paper no. 551 presented at CORROSION/96, March 24-29, 1996, Denver.

19. Wolfson, S. L., Materials Performance, Vol. 33(2),1994, p.22-28.

20. Smith, S. N., Schrieber, C. F., and Riley, R. L., "Supplementary Studies of the Galvalum III Anode - Exposure Time and Low Temperature", paper no 35 presented at CORROSION/77, March 14-18, 1977, San Francisco.

21. Schrieber, C. F. and Murray, R. W., Materials Performance, Vol. 28(7), 1988, p.70.

22. Haney, E. G. and Kurr, G. W., "Seawater Testing of Aluminum Alloy Anodes Containing Zinc, Indium and Cadmium", NACE Northeast Regional Meeting, Hartford, CT, October, 1975.

23. Houghton, C. J. and Ashworth, V., "The Performance of Commercial Zinc and Aluminum Anodes in Hot Sea-Bed Mud", paper no. 81 presented at CORROSION/81, April 6-10, 1981, Toronto.

24. Smith, S. N., Reding, J. T., and Riley, R. L., Materials Performance, Vol. 17(3), 1978, p. 30.

25. Kiefer, J. H., Thomason, W. H., and Alansari, N. G., "Experiences in Retrofitting Sacrificial Anodes in Offshore Arabian Gulf," paper no. 735 presented at CORROSION/98, March 22-27, 1998, San Diego.

E. Quality Assurance

1. Chemical Manufacturers Association Publication "Mechanical Integrity Supplement to the Maintenance Excellence Guide" 1994

2. API Recommended Practice 75 (RP 75) "Recommended Practices for Development of a Safety and Environmental Management Program for Outer Continental Shelf (OCS) Operations and Facilities (Section 8 – Assurance of Quality and Mechanical Integrity of Critical Equipment)".

3. Center of Chemical Process Safety Publication "Implementing Process Safety Management Systems"

4.   Center of Chemical Process Safety Publication "Technical Management of Chemical Process Safety"

F.   **Design, Monitoring, Inspection and Testing**

1.   Code of Federal Regulations: 30 CFR 250.142 (1989) "Periodic Inspection and Maintenance of Offshore Structures"

2.   American Petroleum Institute: API RP 2A (1991) "Planning, Designing, and Constructing Fixed Offshore Platforms - Section 13 "Inspection" and Section 14 "Surveys"

3.   Nace Standard RP0176-83 (1983) "Recommended Practice for Corrosion Control of Steel, Fixed, Offshore Platforms Associated with Petroleum Production"

4.   Wang, W., Hartt, W. H., and Chen, S., "Sacrificial Anode Cathodic Polarization of Steel in Seawater," Corrosion, Vol. 52, 1996, pp. 419-427.

5.   W. H. Hartt, Chen, S., and Townley, D. W., "Sacrificial Anode Cathodic Polarization of Steel in Sea Water - Part II: Design and Data Analysis," Corrosion, Vol. 54, 1998, pp. 317-322.

6.   Townley, D. W., "Unified Design Equation for Offshore Cathodic Protection," paper no. 97473 presented at CORROSION/97, March 9-14, 1997, New Orleans.)

7.   "Cathodic Protection Design," DnV Recommended Practice RP401, Det Norske Veritas Industri Norge AS, 1993.

8.   "Corrosion Control of Steel-Fixed Offshore Platforms Associated with Petroleum Production", NACE Standard RP 0176-94, NACE International, Houston, 1994.)

9.   H. A. Humble, Corrosion 2 (1948) pp 358 – 370.

10.   30 CFR 250.122 – Best Available and Safest Technologies (BAST).

G.   **Bio Fouling**

1.   J. A. Beavers, G. H. Koch and W. E. Berry, "Corrosion of Metals in Marine Environments", MCIC Report/ July, 1986.

2.   W. H. Hartt, W. Wang and T. Y. Chen, "Critical Questions Pertaining to Deep Water Cathodic Protection", Corrosion 89, paper 576, NACE International, Houston, Texas.

3.   K. P. Fischer, W. H. Thomason and S. Eliassen, "CP in Deep Water: The Importance of Calcareous Deposits and the Environmental Conditions", Corrosion 96, paper 548, NACE International, Houston, Texas.

4. B. J. Little and P.A. Wagner, "The Interrelationship Between Marine Biofouling and Cathodic Protection", Corrosion 93, paper 525, NACE International, Houston, Texas.

5. G. W. Swain and J. Patrick-Maxwell, "The effect of Biofouling on the Performance of Al-Zn-Hg Sacrificial Anodes", Corrosion 89, paper 289, NACE International, Houston, Texas.

6. N. Palaniswamy, P. F. Auto, S. Rao and A. Bhardwaj, "In situ chlorine generation for controlling biofouling of offshore structures", CORCON 97, Corrosion and its Control II, Elsevier Science BV, 1998, pp 482-492.

WORKING GROUP ON PIPELINES

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Summary

The Working Group consisted of about 20 people from different parts of the pipeline industry, including pipeline companies, regulators, researchers, vendors/suppliers, and consultants. In this report, the discussions of the Working Group on Pipelines are presented and summarized, the recommendations of the Working Group are outlined and priorized, and those recommendations considered to be the most important are listed.

Those participating in this Working Group considered the top-rated requirements of the pipeline industry to be:

- C.P. design guidelines for new deep water pipelines.

- For existing infrastructure:
  - a state-of-the-art review on in-line inspection,
  - a comparison of pigging and hydrotesting performance,
  - development of standards for performance of pigs, and
  - characterization of pressure spectra in operating pipelines.

- Corrosion modelling.

Introduction

The pipeline industry consists of a team of several industries, including the steel industry, the inspection industry, corrosion specialists, the coatings industry, and regulators. In addition, a consulting industry has developed to serve the needs of the pipeline industry. The 20 participants in this Working Group included pipeline companies, regulators, researchers, vendors/suppliers, and consultants, so that most segments of the pipeline industry were represented.

Important industry-wide trends were described as including aging pipelines, new pipelines being designed and constructed in "hostile" environments, less R&D funding, and increased public awareness. With these trends as the background, the main purposes of the Working Group were to communicate with others in different parts of the pipeline industry, to identify genuine gaps in knowledge, and to identify the top R&D priorities. Specifically, the objectives of the Working Group on Pipelines were, firstly, to identify current issues, secondly, to priorize these issues, and thirdly, to develop a set of recommendations.

The Group focused on six main topics:

- Aging Pipelines
- Deep Water Pipelines
- Corrosion
- Inspection
- Coatings
- Novel Pipeline Design/Construction

The Working Group discussions on each of these topics are summarized in the following sections of this report.

Aging Pipelines

The discussion on aging pipelines focused on aspects related to safety, life extension, and accident prevention, including monitoring and inspection to predict internal and external corrosion. It is important to establish reliable procedures for rehabilitation of existing pipelines, repair of coatings and retrofitting of cathodic protection systems. It is also important to establish criteria for indicating the need to retrofit C.P. systems. In addition, the need for technology for inspection of coatings was identified.

Deep Water Pipelines

Aspects of deep water pipelines that were discussed included insulated pipelines, pipe in pipe, and dynamic catenary risers. Cathodic protection of deep water pipelines was highlighted as an important consideration, including design criteria, electrochemical current efficiency, the utilization factor for bracelets, and the effect of water depth. On older, deep water pipelines, it can be very difficult to assess the level of C.P. protection.

Various standards that cover deep water pipelines were mentioned, e.g., NACE RP0176-94 on corrosion control of steel fixed offshore platforms associated with petroleum production, NACE RP0169-96 on control of external corrosion on underground or submerged metallic piping systems, DnV RP B401-1993 on cathodic protection design, and CSA Z662 for oil and gas pipelines. MMS pipeline regulations 49CF192, 49CF195, and 30 CFR 250 Subpart J were mentioned, along with those of the Korean Gas Safety Corporation (KGSC) in Korea, the Health and Safety Executive in the U.K., and the National Energy Board in Canada.

Corrosion

About 50% of pipeline incidents are caused by corrosion, so that it is very important to have the

capability to predict line condition and to predict leaks caused by corrosion. In addition, it may be useful to consider a specific corrosion allowance in the pipeline design. In this respect, communication between the pipeline operator with the pipeline designer can be quite important.

Preferential areas for failures were identified as the splash zone of risers, where pin hole leaks sometimes occur. To control corrosion in the splash zone, special attention for maintenance is required. The requirements to control external corrosion were compared for buried vs. above-ground lines. For offshore pipelines, the importance of modelling to optimize cathodic protection design and maintenance was discussed, as was the significant role of water depth.

Modelling and predicting internal corrosion is an important aspect of achieving reliable operation. For flow lines, internal corrosion can take the form of channeling corrosion, usually on the bottom of the pipe. It is important to select the correct inhibitor formulation and to use a dose that results in $360°$ protection. Correct inhibitor selection and dosing are particularly important in multiphase pipelines containing H_2S, CO_2, O_2, and H_2O.

A database of corrosion and failure data can be a useful source of information for documenting historical performance, identifying trends, and predicting future problem areas. Databases can be particularly useful if a common approach is used in different divisions of a company. In particular, for offshore pipelines, it could be helpful to correlate failure statistics at depths greater than 200 feet and at depths less than 200 feet.

Erosion is another form of internal degradation that can occur.

Mechanical damage can lead to fatigue and catastrophic failures.

Inspection

Much of the discussion on inspection focused on risers. Like other parts of a pipeline system, risers should be designed so that external corrosion is controlled. Notwithstanding the importance of designing for corrosion control, risers in J tubes are not cathodically protected. A database of corrosion performance of risers can be helpful in managing corrosion control. Aging risers and sleeve risers are both important to inspect, but both present their own difficulties from the inspection perspective. Particular attention should be paid to inspection of the interface between neoprene and paint.

The importance of establishing state-of-the-art technology for inspection of risers was emphasized. Risers are difficult to inspect, there is considerable variability of ILI data, and false positives are frequently obtained. Pigging requires that the riser be shut in, and pigs can become stuck in risers. The specific type of technology used for ILI of risers can be quite important; e.g., magnetic flux leakage (MFL) pigs identifies magnetic flux leakage patterns. For a pig to be genuinely useful, the length and depth of defects should be accurate to within ±10%, with an

85% confidence rate. The inspection technology that is used should have the capability to assess corrosion in areas where third-party damage has occurred. ISO 9000 certifies the paper documentation, but does not ensure acceptable performance of a particular type of pig.

Risk-based regulations encourage companies to use advanced inspection technologies. Nevertheless, the "risk" of inspection was acknowledged; the more inspection that is carried out, the greater is the likelihood of finding more corrosion. Using the results of reliable and advanced inspection technologies, risk management procedures can be implemented on pipelines and can result in savings in the cost of insurance, which is sometimes higher than it needs to be, because of the lack of data on actual extreme risks.

Coatings

Girth weld coatings were identified as the weakest part of the pipeline coating system, the part most likely to fail. Coatings over weld overlays can be problematic. Some risers are openly exposed in the high corrosion zone and so must be well coated and cathodically protected.

For high temperature operation, 85°C (160°F) maximum, neoprene coatings are used. Thermal spray aluminum is used for some coatings.

A distinction was made between multiphase flow lines that are MMS regulated and transmission pipelines that are DOT regulated, in the U.S.

For designing the overall coated and cathodically protected pipeline system, a costing model should be developed using a design benchmark for design life and taking into account the aging of the system. The design lifetime is typically about 20 years.

Novel Pipeline Construction/Design

Several questions surrounding pipe-in-pipe protection were aired, particularly the effect of deoxygenation and the possible use of C.P. to protect the carrier pipe if the annular space is flooded. Galvanic effects, the effects of seawater on foam, the behavior of water-logged foam, the effects of fire retardants, and microbiologically induced corrosion (MIC) were all identified as issues that could be usefully studied. Protection of insulated pipe was identified a another issue for study.

Application of corrosion-resistant alloys (CRA's), such as 13% Cr steel and titanium, including combinations of these with carbon steel, was identified as a possible growing trend in the future, although coatings for CRA's and fatigue of CRA's are subjects on which more data are needed.

There is a need to identify the characteristics and limitations of dynamic pipelines with vortex-induced vibration (VIV) flexible joints in water, and the effects of temperature gradients, high stress, and high temperature.

Recommendations

General

- It is essential to ensure that the knowledge base keeps up with the requirements of production. In this respect, collaboration between industry and non-profit organizations, including university and government laboratories doing the R&D, is very important.

- Non-traditional pipeline design and construction should be evaluated to ensure that possible benefits are obtained.

- Characterization of the pressure spectrum of operating pipelines, i.e., frequency, f, and stress ratio, R (maximum stress/minimum stress), should be assessed.

- Use of pressure relief equipment, depending on the pressure spectrum, may be required.

Corrosion

Specific needs of the pipeline industry were identified for:

- State-of-the-art reviews on coatings;
- Guidelines for inhibitor selection with full consideration of flow regimes;
- Internal corrosion modelling and prediction for risk analysis;
- Database containing details on failure analyses;
- Data on isolation of pipelines and separation distance;
- Study of coatings for internal corrosion control in flow lines;
- Characterization of anti-fouling materials, e.g., Cu, and possible corrosive effects on Al and steel;

MMS databases can be used to assess the historical experience with corrosion of risers. A database on failure analyses of flow lines can be used to help evaluate corrosion of other flow lines and to predict lifetime.

Inspection

Specific needs were identified as follows:

- State-of-the-art review on internal and external inspection of risers;
- State-of-the-art review on pigging;
- A means to identify critical areas for inspection;
- Assessment of damage caused by hydrotesting;
- Comparison of reliability of hydrotesting and ILI;
- R&D on variability of data obtained by ILI, between different applications of the same technique and between different techniques, e.g., MFL and UT;
- Standards setting the minimum requirements of a pig;

C.P. Design and Effectiveness on Deep Water Pipelines

The Working Group identified the following needs:

- Technology for corrosion control of thermally insulated pipelines
- Applications of dynamic risers -- VIV suppression may lead to shielding of C.P.
- Assessment of C.P. effectiveness on dynamic risers
- Assessment of C.P. interference using boundary element modelling and including effects of pipeline separation, showing effects of separation in comparison with the 12-inch separation required of on-land pipelines.

Priorized Recommendations

The following are the recommendations listed in order of decreasing priority for each area.

Corrosion

1. Internal corrosion modelling and prediction should be used for risk analysis.

2. Guidelines for inhibitor selection, with full consideration of flow regimes, should be developed.

3. A failure analysis database should be developed for collaborative use between industry and R&D organizations (universities, government laboratories).

4. State-of-the-art reviews on coatings should be prepared.

5. Data are required on C.P. interference/pipeline isolation at pipeline crossings.

C.P. Design Effectiveness on Deep Water Pipelines

1, Corrosion control of thermally insulated pipelines requires study.

2. Methods to protect dynamic risers should be established.

Inspection

1. State-of-the-art reviews are required on:
   - Pigging
   - Riser inspection - internal and external

2. Standards for ILI are required, establishing the minimum requirements of a pig.

3. Identify critical areas for inspection.

Reliability

1. Compare reliability of hydrotesting and ILI.

2. Pressure spectra of operating pipelines should be clarified.

Conclusions

The top-rated requirements of the pipeline industry are considered to be the following:

- C.P. design guidelines for new deep water pipelines;

- For existing infrastructure:
  - A comparison of pigging and hydrotesting performance,
  - Development of standards for performance of pigs, and
  - Characterization of pressure spectra in operating pipelines; and

- Corrosion modelling.

MATERIALS STATUS AND DEVELOPMENTS FOR OIL AND GAS INDUSTRY OFFSHORE, TOPSIDES

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ABSTRACT

The impact and evolution of technology as related to materials and corrosion control are reviewed for oil and gas topsides design. The current practices in materials selection are discussed for sea water systems, fire water systems, process piping, water and gas injection, topsides equipment, valves, and manufacturing and testing. The use of composite materials on topsides is described for cost savings. The relationship between various conceptual options and total project costs is also reviewed. Finally, the impact of industry specifications in relationship to offshore production is discussed. The decisions for developing and operating offshore production systems require an appreciation of all of these factors.

RECOMMENDATIONS

A list of recommendations was compiled at the workshop.

1. In deep water offshore structures, topsides components have a high multiplier for weight reduction, thus a high potential for cost reduction. Examples of new applications in composite materials are in production and drilling risers, topsides flowlines, deck structures and process systems which have the potential for significant weight savings. Use of high strength light metals such as titanium alloys also applies.
2. Technology development by equipment or component manufacturers can not be economically justified for low cost, critical items. Two examples might include developments in topsides bolting and corrosion inhibitors in gas phase service.
3. Improved technology transfer is needed in the manufacturing and use of duplex stainless steels and super-austenitic stainless steels. Future anticipated usage of even more highly alloyed materials will require improved technology transfer.
4. Fiber reinforced polymers (FRP also known as GRP) require a more complete data base on applications, models for predicting durability, and QA/QC developments. Standardization for dimensions is critical for industry application.
5. The deWaard and Millliams prediction methodology for CO_2 corrosion is universally used. Additional work to further define its application limits will benefit the industry.
6. Changes in offshore processing require a response in corrosion control. One example is the increased use of "inert gas" containing high oxygen contents generated on offshore facilities.
7. The field of corrosion science should address the "people problem" in materials selection and corrosion control, as an important aspect of corrosion management.

INTRODUCTION

This paper briefly addresses technical, economic and specification issues related to materials and corrosion control in offshore topsides construction and operation. The overview provides many generalizations used in design. However, the economic impact of new developments is large, and each project will need to examine these issues, specifically for that project. The optimum choices may vary, even for apparently similar production conditions.

While the intent is to concentrate on topsides oil and gas production issues, there is considerable overlap and interdependence with subsea production equipment, as well as offshore fixed and floating structures.

ENGINEERING DEVELOPMENTS

Compared with the situation 20-30 years ago, a silent revolution has taken place regarding topside material selection on oil and gas producing platforms. At that time carbon steel, mostly plain carbon steel, was dominant in sea water, fire water, process piping, and equipment applications throughout the industry. Precautions were taken against corrosion in seawater and in firewater, however one can imagine the service life and efficiency of internally painted, galvanized, or concrete lined piping. For example, some process piping suffered heavy CO_2 corrosion. By use of costly inspection in these facilities, many pipes were replaced in due time, while some were not, resulting in failures. Quite often the fire water systems were not working satisfactorily due to plugging of pipes and nozzles. The sprinkler heads were especially plugged with corrosion products. Preferential corrosion of piping butt welds was quite usual in process flowlines and produced water lines.

The stainless steels AISI 303, 304, 316 and 321 were then accepted for use in piping of chemicals and hydraulic oil, and even in sea water systems. External corrosion attack soon appeared, and only 316 proved to be resistant to the offshore atmosphere. Grade 321 stainless steel, which is intended for possible elevated temperature excursions, is less corrosion resistant than 304 because of the formation of the TiC, and because of reduced amount of dissolved nitrogen and chromium.

The CuNi alloys were also taken into use to cope with the corrosion of the sea water. However, the Cu alloys are very sensitive to sea water velocities. General corrosion and erosion-corrosion occur at high velocities (v> 3m/s, 10 ft/s) and pitting corrosion at stagnant conditions.

The exotic materials came into use in the eighties and nineties. The exotic materials include 22 Cr and 25 Cr duplex and 6 Mo stainless steels, Ni base austenitic alloys, and Titanium alloys. The basis for the new materials was the good corrosion resistance experienced with Ni based superalloys in the chemical and aircraft industries, such as Inconel 625, 718, Hastelloy B-2 and C-276. Secondly, even though duplex stainless steels were developed before World War II, they did not become fully weldable until the foundries were equipped with modern melting techniques (AOD or vacuum refining). This new melting technology which came into use in the mid seventies formed the basis of production of controlled and very clean melts, enabling production of high alloyed duplex or austenitic stainless steels.

External Stress Corrosion Cracking

One problem with the 300 series stainless steels and the new austenitic and duplex materials is the risk of external stress corrosion cracking (SCC) caused by the chloride rich atmosphere offshore. The Ni content plays an important role and the lowest resistance is experienced at about 8 % Ni linked to the stacking fault energy of the lattice.[1] The duplex stainless steels have a much better resistance against SCC due to 50% ferrite content of the structure. Exposed to offshore atmosphere, the 22 Cr duplex shows resistance to 230°F (110°C). Above 230°F (110°C), 6 Mo or 25 Cr should be used. The limit for the 316 stainless steel is about 140°F (60°C).

Sea Water Systems

For a number or reasons, the 6 Mo and 25 Cr stainless steels were not as corrosion resistant as first assumed during their introduction in the eighties. A minimum PRE value (PRE is defined as PRE = % Cr + 3.3 x % Mo + 16 x % N) of 40 was not specified for these alloys, which was a big mistake. Further, the maximum operating temperature of 95°F (35°C) recommended at that time was not followed. The cooling water temperatures were sometimes greater than 120°F (50°C). Also, these new materials have excellent properties provided they are manufactured correctly, but their sensitivity to incorrect heat treatment manifested itself by pitting and crevice corrosion. Presently, the recommended materials for sea water service below 60°F (15°C) are 6 Mo and 25 Cr duplex stainless, and greater than 60°F (15°C) Ti or fiber-reinforced polymer (FRP). However, due to unexpected problems with the FRPs, Ti is the preferred material. The problems with FRP are related to bad design (insufficient supports, vibrations and water hammering effects), handling damages at sites, manufacturing failures and mistakes introduced by hydrostatic pressure testing.

It is possible to use 6 Mo or 25 Cr duplex piping above 60°F (15°C), up to 95°F (35°C), if all crevices are weld overlaid by Inconel 625, or the flanges and threaded connections are from more crevice corrosion resistant alloys. This can be achieved by use of superaustenitic material such as 654 SMO or UNS S34565. The PRE value for these superaustenitic materials is above 42, with a high amount of nitrogen and manganese. The availability is improving and today it exists as casting, forging, fitting and pipe (welded and seamless). The steel is welded by Thermanit Nimo C or EL-NiCr 22Mo16. The austenitic structure also allows cold bending and flaring.

The elements nitrogen and manganese make the material very strong and due to the austenitic structure the material is given more favorable allowable stress than 25 Cr duplex (according to ASME B31.3) This makes the material attractive for high pressure corrosive process piping systems. See also Figure 1 for a comparison between different allowable stress and cost for the various grades of CRAs.
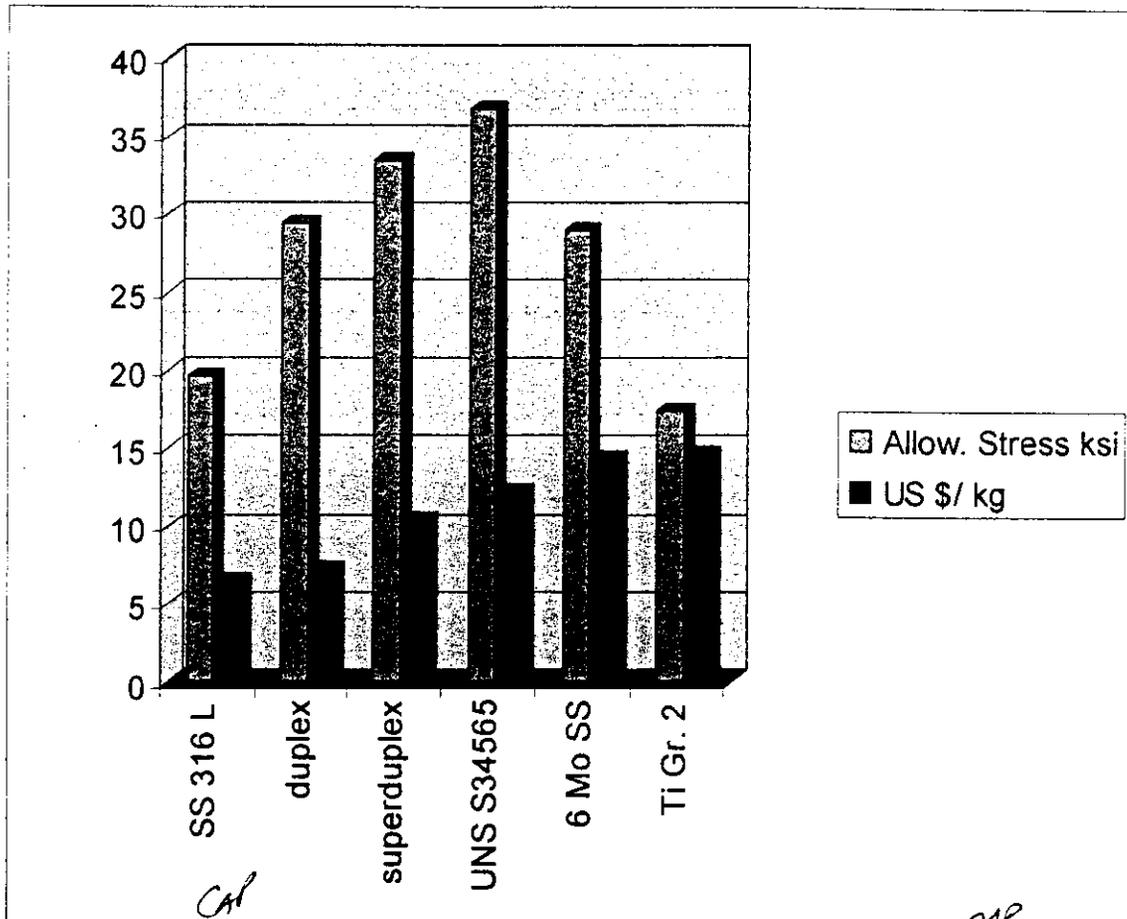
Figure 1. Cost relations and Allowable Stress. Note: Cost of Titanium is related to Volume

Fire Water

Materials selection can be similar for fire water and sea water systems. The sprinkler system is filled with sea water. The small nozzles do not allow for any corrosion products to pass, and the piping must be from Ti or FRP due to operation temperatures above 60°F (15°C). For the dry sections of the deluge system, galvanized carbon steel is the least expensive alternative.

There is one important difference between the firewater and seawater systems. Fire water pumps are pumping only during monthly testing. For the rest of the time the dedicated fire water pumps are on a standby mode and the system is stagnant. For the stagnant conditions, oxygen reacts with steel to form hydroxyl ions in the first two or three days, and hence, no further corrosion will take place after this initial phase. Therefore, fire water systems are designed for fire and for testing, which is much less corrosive than with utility seawater which is flowing every day. Thus, "the ring main" can be from carbon steel for a service life in excess of 30 years. Because corrosion scale from the c-steel ring main and laterals has the potential for clogging the nozzles during a test or fire, FRP fire water piping is the standard for many companies because of reduced maintenance and equal or better fire performance.

Process Piping

Upstream of oil/gas separation, the fluid can be very corrosive to carbon steel. The reasons are high temperatures, water in the liquid phase which contains CO_2, H_2S and chlorides. Prediction models for CO_2 corrosion are widely used, and the most important one is based on modifications of the deWaard and Milliams monograph.[2] As a rule of thumb, if the calculated annual corrosion attack times the design life is less than 0.125" (3 mm), then carbon steel is used. If more than 0.125" (3 mm) corrosion allowance is needed, then the standard 22 Cr duplex material is most probably the correct material. This material is strong, enabling low wall thickness and reduced weld work. Even smaller wall thickness can be obtained with 25 Cr duplex or the new superaustenitic material, but the cost needs or should be considered. A good alternative is to have piping in 25 Cr or superaustenite, and valves in 22 Cr since there is much better availability of 22 Cr valves.

Downstream of separation, the gas lines are often from stainless steel due to CO_2 and water. The crude oil lines can be of standard carbon steel because of the inhibiting effect of some crudes. For the produced water, carbon steel suffers from heavy corrosion especially if CO_2 is present. The most likely corrosion is located at bends, transition zones, and at welds. With un-alloyed filler material, the welds will be less noble than the base material. Often the weld metal corrodes selectively. To avoid this situation, low alloy filler metal is used in the root and hot passes consisting of 0.8 – 1 % Ni or 0.4-0.8 % Cu plus 0.5 – 1 % Ni. However, the results of this practice are disappointing. The heat affected zone (HAZ) on both sides of the weld can be galvanically attacked resulting in deep narrow grooves.

Therefore, 22 Cr is used in the high pressure section(s) and 25 Cr or 6 Mo in the low pressure part of the system. The reason for having the most noble alloy in the low pressure section is the risk of introducing small amounts of oxygen into the fluid. A small amount of oxygen can cause the electrochemical potential to rapidly increase causing pitting and crevice corrosion in 22 Cr, while 25 Cr and 6 Mo will stand a higher oxygen content. FRP is a very attractive candidate for the low pressure sections provided the design temperature is less than 155-175°F (70 – 80°C).

Water and Gas Injection

For gas injection carbon steel is the natural choice when the gas is dry (no water). For water injection, carbon steel is acceptable from a corrosion standpoint when oxygen is depleted. For the high pressure parts, it is often economical to use a 22 Cr duplex material due to a reduced wall thickness. The valves however, are 4-5 times more expensive in duplex than in carbon steel. Therefore, carbon steel valves and duplex piping are recommended for high pressure systems.

The standard 13 Cr and 410 stainless steels have very mixed performance in seawater injection service, especially downhole, and these materials are not frequently chosen for topsides piping. The alloys are susceptible to pitting in all but fully deaerated seawater, and repair welding is not done because of requirements for post weld heat treating. However, new super 13 Cr steel has more potential for process piping. The lean chemistry makes it relatively inexpensive. With yield strength in excess of 61 ksi (420 Mpa), it enables use of thin-walled piping. The super 13 Cr is weldable for use to –50°F (-45°C) and has much better corrosion resistance in waters. On

topsides applications however, 13 Cr must be surface protected (painted) due to the offshore atmosphere. Maintenance cost therefore must be considered.

Equipment

Vessels, pumps and equipment are fabricated from materials compatible with the connecting piping. However, low pressure vessels may be internally coated and equipped with anodes. For high pressures, the most economic concept is high strength carbon steel plate with a corrosion resistant alloy cladding. The carbon steel may have yield strengths ranging from 52 ksi (360 Mpa) to more than 70 ksi (490 Mpa) with excellent weldability and low temperature impact properties (down to – 50°F, -45°C). Clad piping is also available for pipe lines.

Some manufacturers prefer applying internal weld overlay after construction of the vessels. Using a two pass weld overlay process with Inconel alloy 625, iron dilution in the overlay can be controlled. An iron content as low as 7 % can be easily obtained at the outer surface in overlays that are 0.125 – 0.2" (3-5 mm) thick. This provides a very corrosion resistant surface for high pressure service.

Valves

Much attention is paid towards manufacturers of valves. This is due to mixed experience with valves, and the fact that these items consist of materials from various sub-suppliers and manufacturers. Trim material requires more consideration in order to increase mean time to maintenance and or repair. In addition to the metals, gaskets and sealing materials require consideration.

Manufacturing and Testing

One important reason that many "new materials" did not behave as expected was because of manufacturing. Many manufacturers are not capable of producing "sound" materials due to lack of knowledge, equipment, procedures and systems and quality control.[3] These new materials have low tolerances regarding manufacturing routes. Also, the corrosion resistance is not as good as demonstrated through short term laboratory testing. This is valid both for crevice, pitting and stress corrosion testing. Although the number of reported failures is small compared to the actual number of items installed, the use of these new materials was questioned early in the nineties. Occasionally, manufacturers use one production routing for material qualification, and a different routing for actual production.

Future Look Ahead

For low pressure sea water systems, Ti will most likely be the dominant material provided it is not cost-prohibitive. The 6 Mo and 25 Cr will survive as materials for cold sea water systems (less than 60°F, 15°C). The use of superaustenitic materials for "crevice materials" as flanges and threaded connections may extend the temperature limit to 95°F (35°C). Also the FRPs can gain popularity for a number of different applications. Use of anodes (cathodic protection) will be considered for both carbon steel and low alloyed stainless steel sea water piping, equipment, and

valves to keep the costs down. For process piping upstream of the separation stage and downstream of separation for produced water lines, the high strength 22 Cr and 25 Cr will be dominant. The new superaustenitic 654 SMO or UNS S34565 may become economically attractive for weight savings in high pressure service on floating units.

For piping of un-processed fluids, research work in CO_2 corrosion may result in solutions based on use of inexpensive carbon steel and injection of effective film forming inhibitors, pH stabilizers or glycol and the like. However, these inhibitors may have cost and environmental impacts.

In the future, only qualified and serious manufacturers should be used for manufacturing of critical materials. The material engineers will face more difficult questions and problems than ever before. These engineers have to correctly use corrosion calculations, propose materials based on lowest life cycle cost, be knowledgeable about field experience, document material proposals, possess knowledge about manufacturers and will have to be continually aware of the market situation, and be able to communicate effectively with most other engineering disciplines.

COMPOSITES

As part of the oil industry's efforts to reduce the life-cycle costs of deepwater and marginal field developments, and to improve reliability, considerable attention is being devoted to the evaluation and application of innovative and cost-competitive alternative materials. Although the traditional engineering material for offshore structures is steel, composites materials have been receiving much attention by the oil industry as demonstrated by the many joint industry projects, special meetings, and workshops. Composites offer many potential advantages for marine construction based on low density, corrosion resistance, and excellent fatigue performance. Weight savings offered by composites have a direct impact on platform cost because of the payload premium of offshore structures[4] given in Table I.

Table I. Payload Premium for Deepwater Structures

Concept	Payload Premium, $/lb
TLP	4-7
Semisubmersible	3-5
Ship and SPAR	1-3

In addition, the use of composites permits greater design flexibility for tailoring properties to meet specific design requirements, thus promoting better system-oriented, cost-effective solutions. Also, new innovations are being developed to embed fiber optics and electrical conductors into the composite part to monitor quality during manufacturing, to monitor structural integrity and loads during service, and to obtain operational conditions from remote locations. Although on a one-on-one basis, components made of these materials will most likely be more expensive than an identical, or functionally equivalent, steel counterpart on a performance-equated basis, the economic advantage of composite components can often be demonstrated by examining their impact on reducing system and full-cycle costs.

FRP materials consist of small-diameter fibers of high strength and modulus embedded in a matrix with bonded interfaces which permit the fibers and matrix to form a new material which captures the desirable characteristics of each. The most common fibers are glass, carbon and aramid. Polymeric matrix materials can be thermoset or thermoplastic. The most common polymeric matrix materials are polyester, vinyl ester, phenolic, acrylic and epoxy. Fibers are usually incorporated into the matrix in long continuous lengths but are sometimes utilized as short discontinuous fibers. Only during the last decade the fiberglass industry has started to seriously consider new technologies such as improved resins, reliable connections, selectively using carbon fibers, implementing better quality control and NDT techniques, publishing better design and installation guidelines, and using improved fire resistance formulations and coatings. Therefore, past negative experiences with fiberglass composites should not be used as a basis for judging current materials. As an example, in the past many operators had very disappointing experiences with leaks of fiberglass pipe joints, but recent applications of FRP pipes on platforms such as Heidrun and Ram-Powell have shown that the leak rate of several thousand field joints was less than 0.1%.

Examples of Topside Applications of Composites

Fiberglass composites, and to a lesser extent carbon composites, have also been used by the offshore oil industry in a variety of topside applications. These include storage tanks, pressure vessels, low pressure pipes, structural parts, seals, gratings, fire and blast walls, cable trays, etc. The motives are lower weight, less maintenance, and reduced installation costs. Some specific examples for the offshore topside application of fiberglass composites include firewater piping (Amoco's Valhall, Conoco's Marquette, Shell's Mars), seawater piping (Dubai, Conoco's Heidrun; Norway, Phillips Ekofisk), storage vessels (Conoco's Heidrun, Amoco's Davy/Bessemer), and grating (Shell's Mars and Ram-Powell). Figure 2 shows a picture of FRP piping and grating used on a TLP in the Gulf of Mexico.
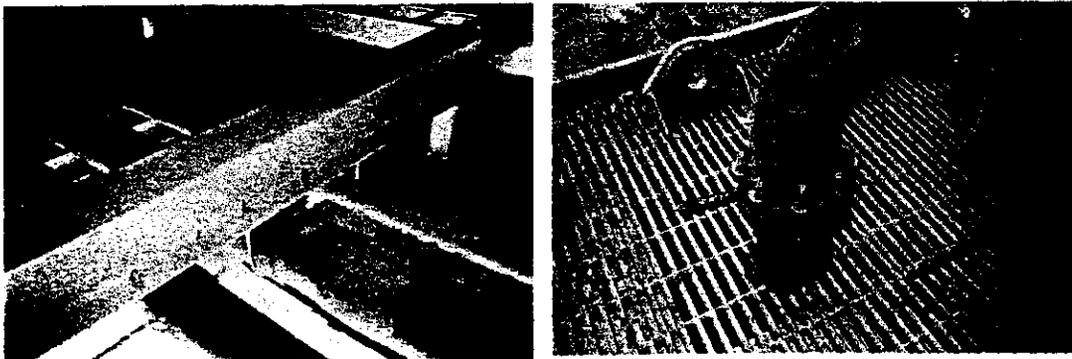
Figure 2. FRP Piping and Grating on a TLP in the GOM

Composites have also been used for many high-pressure vessel applications. Compressed natural gas pressure vessels from glass and carbon fiber composites with a high-density polyethylene liner have been in use for many years. Composite pressure vessels have been developed and qualified for use as mud gas separators (MGS). The primary advantages that composite MGS offer are reduced maintenance due to composite's corrosion resistance, and 50% weight savings over carbon steel.

Composite accumulator vessels have been used for production-riser tensioning systems on the Ursa, Mars and Ram-Powell TLPs as shown in Figure 3. These vessels have a volume of 11,600 in^3 (17.3 inch OD, 82.5 inch length, 365 lb weight) and are ASME code Section X-rated, PR certified for 35 year service life at 3000 psi operating pressure (burst pressure > 15,000 psi). While the weight of these composite vessels was about 1/3 the weight of the equivalent steel vessels, the cost of the composite vessels was actually lower than the steel vessels.

Figure 3. TLP Riser Tensioner Accumulator FRP Vessels.

Although most efforts on composite materials are focused on their applications for deepwater structures, composites have been successfully used for shallow water structures to take advantage of weight reduction and lower maintenance cost. The low maintenance advantage of composites is becoming important for unmanned platforms. This was illustrated for structures such as Amoco's Davy/Bessemer[5] and Mobil's Galahad platforms[6]. Amoco's Davy and Bessemer mono-tower platform is in 30 m water depth in the North Sea[7]. The 659 tonne mono-tower supports the 350 tonne topsides. The light weight and corrosion resistance of composite materials provided economic incentives for their use in several components on this application.

These components, their size, weight and cost are provided in Table II. While a weight saving of about 33 tonnes (9% of the final topside weight) was achieved which is 68% of the steel weight,

the cost premium was about 42,000 British pounds which is 14% more than the steel cost. Table II does not account for the advantages of the lower weight FRP on installation costs nor the additional painting cost for steel components. The two components most responsible for the higher FRP costs are the fire resistant ladders and gratings. Amoco attributed this high cost (more than 7 times the steel cost) to the restricted procurement time that made it necessary to use a single source of supply. Shell's experience in the application of fire resistant grating and ladders is that the FRP cost is only 3 times the steel grating (FRP grating is 12$/ft^2 vs. $4/ft^2 for steel). By taking advantage of the lower weight and simplicity of installation of FRP grating, Shell experience suggests that the total installed cost of FRP grating is comparable to steel grating. Therefore, the offshore application of fire resistant glass fiber-phenolic grating continues to expand in the Gulf of Mexico as shown in Table III.

Table II. Weight and Material Cost of FRP components used on Davy/Bessemer Platform

Component	Size	Weight, Tonne		Cost, 1000 British pounds	
		FRP	Steel	FRP	Steel
Grating	293 m^2	5.0	10.3	58	7.9
Handrails	339 m	3.0	5.8	44	24
Ladders	49.6 m	0.28	1.6	12	7.2
Office Mod.	120 m^2	1.25	5.2	84	96
Equipment Mod.	154 m^2	1.5	6.7	87	96
Tool Room	28 m^2	0.6	2.6	12	4.0
S.S. Diesel Tank	24 m^3	2.35	3.5	18	28
S.S. Lube Tank	0.85 m^3	0.02	0.43	1.8	10
Two S.S. Utility Tanks	1.03 m^3	0.24	0.84	3.3	19
Open Drains	192 m	0.27	3.9	13	6.0
Caissons	132.5 m	1.1	5.7	15	6.2
Total		15.6	48.7	347	305
Fuel Loading Arm	12 m	0.15	No steel option	20	

The use of composites for structural applications is attractive in terms of weight savings. Therefore efforts are underway to develop this application. Both sandwich and pultruded composites are being considered for manufacturing these structural beams. Two fabricators, Coflexip and Strongwell, are active in this area. Tests by Coflexip have shown that composite beams can be built with more strength and more fire resistance than steel, which could have special applications in rig floors and hull support. In addition, the application of composites for load bearing floors, bulkheads, helidecks and living quarters can take advantage of the current development efforts of composite bridges.

Table III. Application of Fiberglass-Phenolic Grating on Deepwater TLP Structures

Platform	FRP Grating Area, ft^2
Mars	88,000
Ram Powell	99,000
Ursa	190,000

Barriers to the Application of Advanced Composites

The expanded application of composites in the oil industry continues to face technical, financial and emotional barriers that must be overcome to allow the full potential of composites to be realized in critical offshore applications. Solutions to these barriers involve developing a more comprehensive design, manufacturing database to allow competent risk assessment, establishment of reliable cost structure for both components and systems, and educating offshore contractors and suppliers to provide them with sufficient confidence to design and use these new materials[8].

The successful commercialization of advanced composite components requires that development programs incorporate input from all participants including material supplier, manufacturer, engineering contractor, user, and regulatory agencies. Advanced composite applications can often draw on the knowledge and extensive database developed by defense and aerospace companies. Any successful development must include extensive economic analysis to ensure that the results are aligned with the needs of the oil industry, particularly deepwater development. Therefore, the key to the successful development of composite components for the offshore oil industry is project implementation within a value chain partnership including owner, designer, material supplier, fabricator, regulator, and system integrator.

Design and Manufacturing Considerations

Unlike other commonly used offshore materials, such as steel, that are homogeneous and isotropic, fiber reinforced composites are microscopically inhomogeneous and orthotropic. As a result, predictions of stresses, strains, and deformations in composites are more complex. Fortunately, the advances that occurred in design and analysis of composites during the last decades resulted in development of many software packages that are capable of conducting analysis of very complex composite geometries. Also, unlike metals where failure predominantly occurs as a result of crack development and growth, composites fail because of multiple damage mechanisms. These damage mechanisms include fiber fracture, matrix cleavage, matrix shear, matrix plasticity, fiber/matrix debonding, fiber microbuckling, and interlaminar debonding. Damage mechanisms of composites are not only impacted by thermal and mechanical loads, but they are also influenced by environmental sensitivity such as water absorption. Sometimes, damage of composites can result in a redistribution of stresses and, thus, increases the strength. However, the type, extent, and location of damage determine whether load is relieved or intensified.

Since the fire resistance of composites presents a significant technical issue that has limited the use of composites in many applications, major efforts have been directed to address this concern.

In a recent workshop on composites for surface ships and submarines, fire threat was ranked as one of the top concerns among technical issues that included cost, acceptance process, environmental effects/disposal, structural analysis/joints, and large scale validation[9,10]. Fire performance of materials is characterized by their fire growth (ignitability, flame spread, heat release and flashover), habitability (smoke and toxicity), and residual strength (structural integrity). A survey of various commercially available thermoset and thermoplastic composites showed that the phenolic based composite materials offer the best cost-effective fire performance[11]. Phenolic resins have low flammability, low flame spread, high ignition delay, and low heat release rate. In addition, they char during fire exposure, thus, insulating the composite structure and minimizing structural damage. Most phenolic resins evolve water during curing, yielding high void content and weaker matrix, and, thus, limiting their use for primary structural applications. However, efforts are continuing to improve their performance. The poor structural performance of phenolics can be overcome by modifying the phenolic resin with siloxane. This resin system is now being used by Ameron Fiberglass Company for fabrication of pipes for marine applications[12]. Fiberglass composite pipes have been used in firewater systems of many offshore structures. For wet systems, i.e., water is always in the pipe, fire protection is, generally, not required. However, most companies specify fire protection for joints, fittings, and flanges. For dry systems, fire protection is always required.

The risk of fire due to the accumulation of static electricity on FRP components is often raised. Although this issue is over-stated, it should be satisfactorily addressed. Standards do exist such as the United Kingdom Offshore Operators Association (UKOOA) piping document that provides guidelines for the maximum allowable values of resistance to earth and surface resistance. Most newly manufactured FRP components will not meet these requirements unless they contain conducting elements or additives. However, when FRP components are exposed to marine environment, their surface resistivity is reduced to within safe levels. Also, phenolic FRP components have inherently lower surface resistivity which allow them to comply with the requirements. For Amoco's Davy/Bessemer application, a detailed risk assessment identified that a possible hazard could result from venting a plume of hydrocarbon gas which could deposit electric charge on the new FRP components. Amoco showed experimentally that marine conditioning can lower the surface resistivity, dependent on the type and grade of resin. The resistivity was lowered for phenolic grating/ladder material and class 1 polyester handrail system (which uses an Antimony TriHydride (ATH) fire retardant filler). The same level of conditioning was not observed on standard grade polyester resin.

Many non-destructive testing (NDT) techniques have been successfully applied for inspection of composites. Table IV lists methods and their application in detecting different defects in composite laminates. Reliable inspections require reference standards, written procedures, and inspection criteria. Currently, there is no common standard criterion (as is the case with metals) for evaluation of composites. Individual industries circumvent this issue by developing standards for specific applications. Also, the lack of common definition of a defect in a composite component can complicate the interpretation of NDT results. In addition to inspection using the conventional NDT techniques, composites can be inspected using embedded sensors and other monitoring devices. These composites are known as smart structures. Optical fibers and electrical conductors can be integrated into the composite to monitor quality during

manufacturing, structural integrity, loads during service, and operational data from remote locations.

Repair of lightly loaded composite structures is a common practice. Repair of highly loaded structures is feasible, but requires great care to minimize local discontinuities. Carbon fiber reinforced composites have been successfully used for repair and strengthening of metal structures in both civil and military applications. Two steel firewalls on Mobil's Beryl B platform in the North Sea were strengthened using 250 kg carbon fiber composites to improve their blast resistance. The repair was less expensive than other options, and was performed without any loss to production which would have resulted by the required shut down if welding repair was used[13]. Repairs using composites are also being considered for repairs of welds in Shell's Brent D utility shaft ballast water piping system.

Unlike structures fabricated from metal plates, a composite component achieves its form entirely at the time of fabrication. Therefore, the overall integrity of a composite structure is very dependant on the successful implementation of a comprehensive quality assurance program (QAP), particularly when weight limitations and economic incentives require the use of lower safety factors. The basic elements of a QAP include inspection and testing of all raw materials (fibers, resins, adhesives, cores, etc.), in-process inspection of manufacturing processes, and destructive and non-destructive evaluation of fabricated components.

Table IV. Application of Some NDT Techniques

NDT Technique	Defect Type
Ultrasonics	Delamination, Debonding, Porosity and voids
Thermography	Delamination, Debonding
Radiography	Improper fiber alignment, Poor fiber distribution, Broken fibers, Porosity and voids, Matrix cracking
Eddy Current	Broken fibers, Near surface defects
Acoustic emission	Crack propagation

Standards and Regulations

Regulatory agencies for offshore structures recognize that substitution of steel with composite materials has positive effects on both development and operating costs. They are, however, cautious toward composite material introduction on offshore installations because of the restriction imposed by many existing regulations against the use of combustible materials for structural and piping applications. But, subsequent to the Piper Alpha disaster, regulations began to change from prescriptive to performance based/goal setting standards. This combined with extensive effort to develop engineering documentation and standards by many groups such as Marinetech and UKOOA in the UK, SINTEF and OLF in Norway, and CEAC and API in the

U.S. alleviated the main barriers to the offshore use of composite materials on topsides. Goal setting standards allow materials selection to be based on appropriate use of risk assessment and demonstration of fitness for purpose. Most regulatory agencies in the U.S., UK and Norway have started to adopt the goal setting policy, particularly for fire safety[14]. It is, however, recognized that some issues such as toxicity will remain prescriptive based because they are not well understood.

PROJECT COSTS

Costs are a major driver in establishing the directions for future offshore projects. By understanding the factors influencing project costs, a better assessment can be made of future trends in the industry. As project costs rise, the size of the reservoir must be larger to justify development.

Economics are complicated by changing environments in oil and gas production. The price of oil and gas varies, production rates decline with age, the production method may change, the corrosivity reflects these changes, and technology hopefully improves with time. This section will address costs that are affected by materials and corrosion, both in CAPEX and OPEX. In all of the exercises, the total life cycle costs are of interest.

Use of Cost Estimates

Cost estimates are performed for different reasons. In conceptual work, estimates are required to determine development feasibility. The decisions may specify: dehydration or other processing which impact non-manned operation; corrosion resistant alloys; long multiphase pipelines to eliminate offshore process; existing processing rather than new facilities; pipeline corrosion allowances, sour service requirements, and insulation.

Cost estimates for preliminary engineering have additional requirements. These include estimating engineering costs, and preparing a preliminary budget for construction, installation, commissioning, and production.

Cost estimates in detailed engineering are required for the execution of the project and often provide for incentives in performance within the budgets. These must be performed in addition to reviewing the results from previous engineering efforts.

Costs involved with corrosion impact more than just the project corrosion prevention operating costs. They may impact the project indirectly with space and weight requirements, impacts on schedule, or impacts on alternative field layout. Different projects often require completely different philosophies for apparently identical projects. In-depth analysis shows that each is in reality an entirely different entity.

The oil and gas production rate varies with time, as shown schematically for a typical project in Figure 4. The production profiles are a controlled variable in a project. Usually, the rates are high initially, reducing to low values with time. The life of a project is not fixed but depends on the investment and operating costs and price of hydrocarbons. Components in projects can have

varying lives. Some onshore gas wells produce for only one year. Other wells may produce over 15 years, or sometimes much longer. Oil fields generally produce longer than gas fields. Offshore structures may be designed for 50 years.
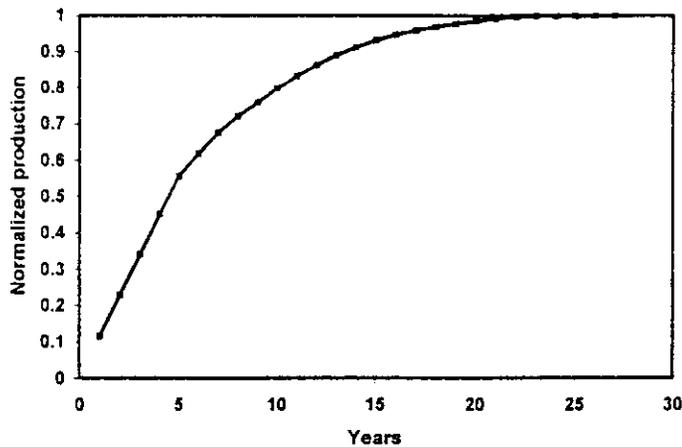

Figure 4, Cumulative Production, Gas Field

The cost of the investment is better known than operating costs. There are key uncertainties, improved cost analyses address these factors. This section of the paper will examine some of the parameters in determining investment and operating costs.

Investment Costs

Investment costs are well budgeted for a project. The value of time is recognized. Also, the time between conceptual cost estimates and purchase may be years, and market conditions change.

For topsides, the space and weight of facilities is important, in addition to the cost of the item itself. The weight includes the equipment and the weight of inventory in the equipment, and the weight increase of the structure to accommodate the equipment. As the water depth increases, the associated cost per ton increases.

Stainless steel facilities are economical for sweet, long life, corrosive production. Small fields with short production lives can be more cost effective in steel construction. In oil production, the early period is non-corrosive because of the low water cuts. The equipment may need to withstand corrosion, or be protected with inhibition, for a short period of time. Technical and economical analyses define the best option. Failure frequency and repair costs, including deferred production, must balance the initial investment costs.

The salvage value is important for short-lived components, such as in production tubing and trees. For long life components, the salvage value is often reduced. The cost of rebuilding old structures is often greater than for obtaining new ones.

For service with declining pressures, a decrease in pressure will permit use of thinner walled equipment at the end of production. This will serve as a corrosion allowance as the pressure declines. A typical example of pressure decline in a producing gas field is shown in Figure 5. Some process facilities anticipate future production, and pressure decline is not applicable.

Corrosion resistant alloys do not require a corrosion allowance. The large cost impact is often balanced by the weight saving. Corrosion resistant alloys generally require less monitoring, and some cost recovery can be realized from this.
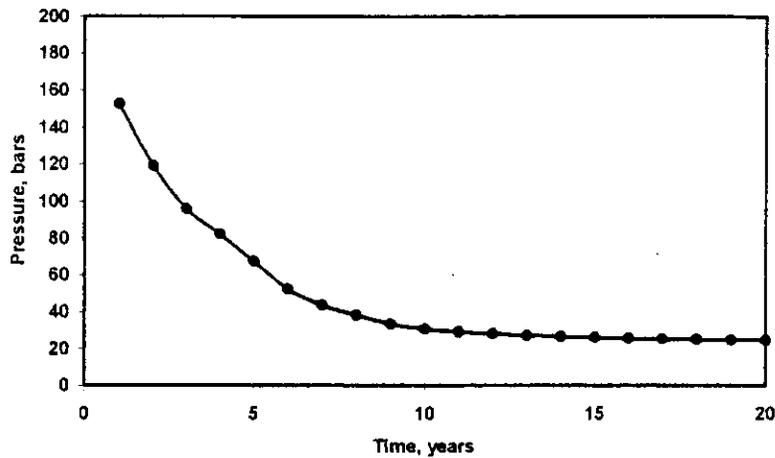

Figure 5, Subsea Manifold Pressure Decline, Gas Field

Availability is sometimes a deciding factor in cost. More emphasis is being placed to bring projects on production earlier. Once procurement is started, delays in the project schedule become expensive. Any construction or assembly done offshore costs much more than onshore.

Reservoir souring has little cost impact on steel construction for topsides. Cracking resistant sour service grades can be obtained routinely, without large cost differences. However, if corrosion resistant alloys are used, the cost impact of souring is large. This is compounded by the difficulty of predicting souring in oil reservoirs.

Both solution pH and chlorides are being promoted as operating parameters in materials selection of steels and corrosion resistant alloys. In new projects, the chloride content and the water alkalinity must be estimated to decide between alloys. For oil production such predictions
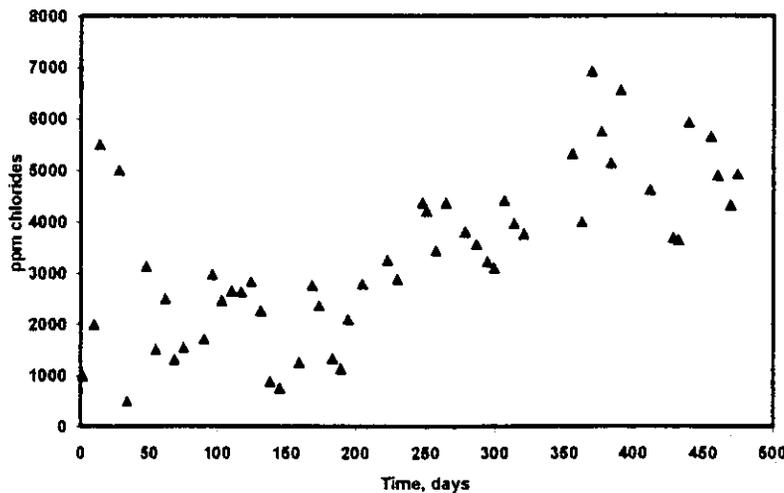
Figure 6, Chlorides in CMS Water, 1993-1995

can be made, but for gas production, the fraction of formation water produced is variable over the age of the field, as shown in Figure 6. The chloride content is indicative of the production of formation water. Consequently, a low alkalinity and high chlorides must be assumed for gas production service in the design phase, and the fine tuning for materials selection (cost savings) using chlorides and alkalinity can not be done.

Production Costs

Operating and repair costs have a broad level of diversity. The time at which repair or replacement is required has an influence on overall cost.

The cost of labor is variable. An offshore man-year may be ½ to ¾ of a million dollars in the North Sea, whereas it may be an order of magnitude lower onshore. The cost of manpower will depend on salary and benefits, transportation, living quarters, platform space and weight, and design life of the facilities. The industry is moving to more non-manned facilities to reduce these costs.

Pulling cost of tubing depends on design. The cost of pulling onshore wells may be a few thousand dollars. On minimally designed offshore facilities, a rig or snubbing unit is required, with a potential cost of a million dollars to replace a single string of tubing. Since production rate decreases with time, earlier replacements result in greater lost or deferred production. An oil well may produce 20 times more initially than toward the end of field life. Production profiles are estimated for projects, and deferred production costs can be calculated.

What can you do for a million dollars?

- Replace tubing for 1/2 to 1 subsea well
- Replace tubing for 1-2 non-manned platform wells
- Buy corrosion inhibitor for oilfield for 1/2 - 1 year
- Buy 5" 13 Cr tubing for 3-4 - 10,000 foot wells
- Buy nickel alloy tubing for 1/5 of that well
- Repair 1/2 of corrosion inhibitor distribution system in North Sea
- Repair 1/15 of a North Sea separator from unexpected corrosion
- Hire 4 man years work from corrosion engineer

costs for some generic remedial measures.

Repairs in wells may be inexpensive, but restricted flow in tubing can result in deferred production. The listing above describes relative

When facilities are shut in for other reasons at a higher frequency than required for corrosion, deferred production costs can not be attributed to corrosion. For example, gas production systems are serviced during low demand where sufficient production is provided by only a fraction of the field. Another example is pulling tubing to retrieve subsurface pumps. The cost of pulling the tubing and associated deferred production is not assigned to tubing deterioration, since tubing may be replaced, but is pulled before it deteriorates. The deferred production cost is assigned to the replacement of the electrical submersible pumps. Unexpected failures incur an additional deferred production related to the time to mobilize repair equipment.

In oil production, the initial period of field life is non-corrosive, as depicted in Figure 7. Properly drilled and completed oil wells into a new formation will initially produce no water. Water production rate slowly increases with time. Oil field experience permits estimation of the rate of increase in water cut. The rate is determined by field size, rate of oil production, water injection rate, field permeability, and other factors. The water production rate is best determined empirically after production starts. In new fields, inhibition may be required only after water cut has reached a critical value, later in the field life. Of course, this is not true for infield wells where water production is realized immediately.

If spares are intended for multiple service, as for production and water injection, then the component must be made from alloys that are acceptable for both services, with cost penalties. This applies, not only to spares, but to all equipment, since the components removed from service become spares.
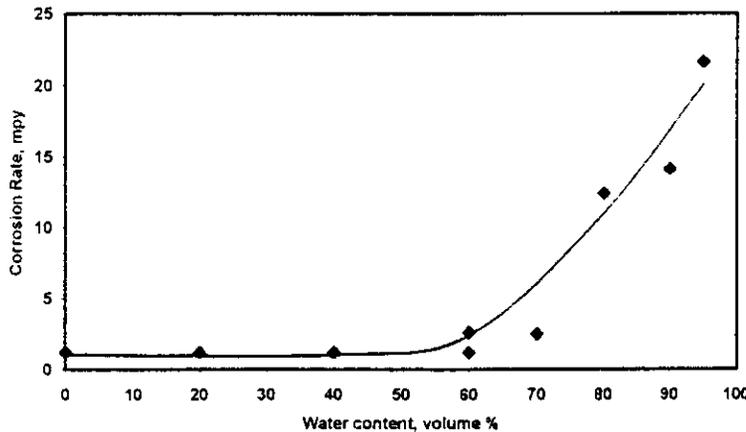

Figure 7, Effect of Water Content on Corrosion of Steel
Mixtures of ASTM Seawater and Field Oil, 25C, 1 bar CO2

Inhibition costs include capital costs and operating costs. The capital costs are: control, injection and distribution hardware, storage weight, space, and tankage, selection program, and corrosion monitoring equipment. The operating costs include: cost of chemical, delivery, manpower to maintain program, housing and transportation, monitoring, and additional selection programs, and technical service. The unit cost of chemical is only slightly variable. The concentration required to control corrosion may vary by two orders of magnitude. An assessment of the required concentration of chemical has more impact on cost of inhibition than does the unit cost of the chemical.

Of course, the chemical costs are primarily determined by the volume of fluid produced, as shown in table V. Gas systems require less chemical, even though the concentrations of inhibitor in the liquids may be a few hundred parts per million. Oil systems may require millions of dollars a year, even at 20 parts per million concentrations.

Table V. Typical Chemical Cost for Different Production

Inhibitor/type	Production	Cost/year, $
200 ppm oil soluble	500 mmscfd gas, 4 bbl liquid/mmscf	50,000
100 ppm water soluble	350 mmscfd gas, 100 bbl condensate/mmscfd	20,000
20 ppm oil soluble	350 mmscfd gas, 100 bbl condensate/mmscfd	90,000
20 ppm oil soluble	120,000 bbl/d oil, 20% water	350,000
50 ppm water soluble	120,000 oil bbl/d, 20% water	150,000
50 ppm water soluble	150,000 oil bbl/d, 80% water	750,000

INDUSTRY STANDARDS AND GUIDELINES

Industry standards and guidelines play a major role in minimizing costs and maximizing safety. These standards and guidelines have provided the needed requirements so manufacturers and suppliers can meet the industry needs with a minimum of diverse requests. These standards and

guidelines are designed to meet about 90% of the industry needs, which leaves the remaining 10% for special applications.

The special application requirements are often those where the technology is unknown and significant research and development is required to obtain appropriate solutions. This R & D is most effective when both the users and the manufacturer/suppliers cooperate to develop the needed new products. As in the past, the developments made to meet the special applications often lead to improved industry standards when the technology becomes available. Examples are sour gas, and deep, hot corrosive well environments.

The sour gas industry provided special material requirements that led to the development of testing procedures, manufacturing methods and material requirements that are now part of the industry standards (MR0175 and API 5CT) and European Federation of Corrosion (EFC) guidelines. The needs identified later by the deep, hot well environments created a new set of problems and solutions. Inhibition often proved ineffective or very expensive for many of the deep wells and available corrosion resistant alloys (CRAs) did not provide the needed strength and little was known about their suitability in the deep well environments. As a result, a new set of technologies and products emerged. These are excellent examples of the benefits of strong cooperative efforts by the users and manufacture/suppliers. The result of this joint effort has led the availability of reasonable cost needed products. These developments also led to improvements in the available test procedures, guidelines and standards. The current special needs will, no doubt, result in similar future new products and modifications to the available guidelines and standards.

Technology and Product Needs

The oil and gas industry is faced with many new technological challenges as a result of (a) deep water oil and gas production environments, (b) corrosive produced fluids containing, chlorides, CO_2 and H_2S and (c) souring of produced fluids after water injection. Extensive efforts are underway in API/ISO, the European Federation of Corrosion (EFC) and NACE International to provide new knowledge on product applicability, and the necessary guidelines, test procedures and standards to meet these new challenges.

The deep water drilling and production activities have led to many new challenges in corrosion protection of offshore pipelines and facilities from corrosive fluids. Sub-sea facilities and long pipelines are often required to handle all of the untreated corrosive produced fluids. The current efforts are largely directed toward developing needed technologies, standards and guidelines so that economic and safe solutions are available for these problems. The choices of protective measures are often limited for the deep water ventures because of limited selections and the high cost of repair when corrosion problems occur.

The offshore production of corrosive fluid containing CO_2 and H_2S continues to be an industry challenge. Much effort is underway in EFC to prepare new or revise EFC 16 and EFC 17 guidelines for selecting a safe, economic solution for the wells and topside equipment. This effort covers a range of problem areas including life cycle prediction, corrosion resistant alloy selection methods, comparison of corrosion protection methods, and development of effective

inhibitors application methods. The development of effective guidelines, which is often followed by standards preparation, provides for the most effective utilization of technology and manpower. The predictive models for CO_2 corrosion and the evaluation of pH effects on corrosion and sulfide cracking (SSC) are good examples.

Reservoir fluids are often modified as a result of water injection to maintain reservoir pressure and improve oil recovery. One of the most important changes is the increase in H_2S content (souring) of the produced fluids, which often occurs many years after water injection begins. This can become a significant problem for offshore environments when the fluid change had not been predicted and high strength materials were utilized in the wells or topside equipment. The souring of the wells after water injection can have a major impact on costs if retrofitting of wells and equipment is required to meet the material's requirements for sour service. EFC 16 guidelines provide a method for considering the effect of pH on the metallic material requirements for these mild H_2S environments. This concept has been used in Europe to permit the use of some previously evaluated high strength N-80 and P-110 casing and tubing for the mild produced fluid environments found in some of these water injection projects. As a word of caution, this concept is generally not applicable to gas production where the unpredictable ratio of formation and condensed water makes pH prediction, at best, very difficult and often impossible.

The material and corrosion requirements for deep, hot and corrosive wells have resulted in a large change in equipment type and availability. These include improved properties and availability of high strength carbon and low alloy steel casing and tubing, and CRAs, and improved inhibition methods. Many of these wells were extremely corrosive because of the high temperatures and concentrations of chlorides, CO_2 and H_2S. Corrosion inhibition often was of limited effectiveness and initially the available corrosion resistant alloys (CRAs) had many limitations. As a result, several years of intensive efforts by the oil and gas industry and alloy manufacturers were required to develop new and improved inhibition methods and CRA technology for the most severe cases. The extensive research and manufacturing developments have led to the availability of a number of high strength CRAs for use in a wide range of environments. The lower cost 13 Cr martensitic stainless steel has proven adequate and has been used extensively for some of the least severe deep well environments. Both EFC and NACE are actively preparing guidelines and standards regarding the environmental limits for these alloys. The NACE activity involves a possible revision to the CRA section of MR0175.

Current Standards and Guidelines Activities

An International Standards Organization (ISO) work group is developing a materials standard for use when H_2S is present in produced fluids. This work group is identified as ISO/TC67/WG7. The objective of this work group is to prepare an international standard for H_2S containing oil and gas production environments. This effort is to combine and modify, as necessary, the guidelines and standards available from NACE and EFC. The first stage in this process is to provide a carbon and low alloy steel standard based upon the EFC 16 and NACE MR0175 documents. The second stage is to prepare a corrosion resistant alloy standard. The third stage is to provide a standard on nonmetallic materials. The timetable calls for completion of the

committee draft of the carbon and low alloy steel standard by June 1999. The second and third stages have been deferred until the carbon and low alloy standard committee draft is completed.

The new standard will provide several new additions to the materials requirements found in MR0175. These additions involve:

1. Modification of the definition of sour environments to include provision for pH modified mild environments,

2. Inclusion of Vickers hardness requirements for welds and heat affected zones,

3. Inclusion of guidelines or standards on hydrogen induced cracking (HIC), sometimes called stepwise cracking (SWC), and stress oriented hydrogen induced cracking (SOHIC),

4. Identification of test procedures in NACE TM0177 and EFC 16 and the acceptance criteria required for high strength carbon and low alloy steels, which are to be used in the pH modified mild environments.

The NACE Task Group T-1F-1 is continuing its efforts to modify the CRA portion of MR0175. This effort involves defining the CRAs by categories rather than by individual items, and by identifying environmental limits for all CRAs. These revisions are planned for completion during 2000.

The available standards and guidelines provide the industry a basis for identifying and obtaining an economical and safe solution for most corrosive environments. The availability of the many material choices and protection methods provided by the guidelines and standards should result in improved economical choices for future projects. Newly identified special environments will continue to drive the technological requirements and subsequently the test methods, guideline's and standard's activities.

REFERENCES

[1] F.B. Pickering , Physical Metallurgy and the Design of Steels, Applied Science Publishers Ltd. London 1978

[2] C. deWaard, U. Lotz, NACE Corrosion 93, Paper No. 69.

[3] T. Havn, A. Morini, H. Salbu, Ø. Strandmyr, Quality Improvements on Duplex and Superduplex Cast and Forged Products for Offshore Applications, Duplex Stainless Steels 1997, 5th World Conference.

[4] M. M. Salama, Some Challenges and Innovations for Deepwater Developments, Offshore Technology Conference, OTC 8455, 1997.

[5] Medicott, P. A. C., Using Composite Materials to Minimize Weight and Maintenance and Maximize Safety, Offshore Platforms'96, 1996.

[6] Salter, H., Stadler, R. L., The Galahad Platform – A State of the Art Minimum Facilities Installation for the Southern North Sea, Offshore Technology Conference, OTC 8201, 1996.

[7] Houghton, C. J., Composites use on Platform Topsides; A recent Case History and Future Prospects," 2nd Int. Conference on Composite Materials for Offshore Operations, U. of Houston, Houston, TX, USA, Oct. 28-30, 1996.

[8] M. M. Salama, Advanced Composites for the Offshore Industry - Application and Challenges, Revue de L Institut Francais du Petrole, Vol. 50, No. 1, pp.19-26., 1995.

[9] Sorathia, U., and Beck, C., Fire Protection of Glass/vinyl Ester Composites for Structural Applications, 41th Int. SAMPE Symposium, 1996.

[10] Sorathia, U., Lyon, R., Gann, R., and Gritzo, L., Materials and Fire Threat, SAMPE Journal, Vol. 32, No. 3, pp. 8-33, 1996.

[11] Sorathia, U., Telegades, H., Bergen, M., Mechanical and Flammability Characteristics of Phenolic Composites for Naval Applications, Navy Programs in Fire and Materials, 39th Int. SAMPE Symposium, 1994.

[12] Folkers, J. L., Fire Resistant Fiberglass Pipe Technology Advances, 3rd Int. Conference on Composite Technology, p. 279, David Hui, ed., University of New Orleans, 1996.

[13] Barnes, F, Carbon Fiber Composites for Strengthening and Repair, Publication of Davenport Management limited, UK, 1997.

[14] Silverman, S. A., Composite Materials for Offshore Operations: Regulatory and Certification Issues, Hart's Petroleum Engineer International, July 1998 issue, pp. 69-73.

CORROSION CONTROL FOR MARINE STRUCTURES AND PIPELINES
in PORTS AND HARBORS

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Harbor and Port Facilities

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Introduction

This paper will discuss the problem and possible solutions to corrosion degradation in port and harbor structures. Port and harbor structures of the United States are part of a decaying infrastructure of reinforced concrete and steel in a marine environment. In many cases these facilities have not been adequately inspected in decades, nor maintained, nor have they been evaluated for continued fitness-for-purpose. This discussion will provide some information about the nature of corrosion damage, testing for damage and various methods to mitigate further corrosion.

The unique features of the marine environment, with radical differences in exposure over the several zones, from atmospheric to splash to submerged and finally to soil interface, cause significant differences in the type, degree and consequences of degradation.

Concrete Structures

The principal mechanisms attacking concrete structures in the marine environment are corrosion of embedded steel, freeze-thaw cycles, sulfate attack, delayed ettringite formation and alkali-silica reaction. In addition, abrasion from high velocity current or accidental impact can lead to corrosion scenarios.

A. Typical Corrosion Damage

1. Cause

Corrosion damage begins when aggressive chloride ions penetrate the concrete cover. Chlorides depassivate the reinforcing steel, leading to corrosion. Since the volume of corrosion products is three to six times greater than the original steel volume, internal pressure develops around reinforcing bars, primarily along outside surfaces where protection is minimal and corrosion is most extensive. Corrosion cracks appear when the internal stresses generated by the expansion of corrosion products exceed the tensile strength of the concrete.

As the corrosion process continues following the opening of the corrosion crack, the corrosion rate may accelerate due to increased exposure to oxygen, chlorides and moisture. With continued corrosion, a closed corrosion spall (delamination) forms and is identifiable as a slightly raised area of concrete wholly or partially encircled by corrosion cracks. Eventually the concrete falls off, resulting in an open corrosion spall.

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2. Structural Consequences

The structural consequences of a corrosion crack are usually minor for conventionally-reinforced concrete components, especially in the atmospheric zone. However, a corrosion crack is usually indicative of a durability problem that may accelerate due to greater exposure to oxygen, chlorides and moisture. The consequences of a corrosion crack in non-prestressed concrete components must be evaluated considering redundancies in design, loading and location, as well as the effect of the dynamic/impact loads (Ref. 9). Some other considerations include:

(a) Steel Reserve – The actual quantities of steel reinforcement used in construction are typically larger than those required by structural considerations. The extra steel is due to a variety of practical design requirements, such as bar layout and spacing and the need to resist high dynamic stresses during installation (i.e. pile driving). Typically, five to ten percent more steel area is provided than is required by analysis.

(b) Actual Loss of Steel at Cracks and Spalls – Theoretical analyses of physical models of deterioration, as well as laboratory tests, indicate that the total amount of steel required to be converted into corrosion products in order to crack the concrete cover is on the order of hundredths on an inch of diameter. Non-prestressed components of marine structures are normally reinforced with large diameter bars, typically from No. 6 through No. 10 (i.e., 0.75 in. to 1.25 in.) Therefore, it should be expected that a relatively small loss in the original diameter would cause cracking and spalling.

(c) Embedment of Corroded Reinforcing Steel – Observations indicate that, in general, reinforcing bars stay well embedded in concrete even after complete spalling of the cover. In most cases, the projecting portion of a reinforcing bar is limited to between ten percent and twenty-five percent of the respective bar diameter. However, in the splash zone, where delaminations may periodically fill with seawater, corrosion may occur on all sides, resulting in a loss of bond.

(d) Point of Maximum Load – Corrosion is often not uniform throughout the length of a member. Quite often, corrosion damage may be limited to the middle or the ends of a member. On piles, the corrosion may be heavy above the waterline but light or non-existent below. This point of maximum corrosion is often quite far away from the points of maximum moments and shear loads in the member, but the reinforcing may be uniform throughout.

As corrosion progresses, eventually an open corrosion spall forms. The pseudo-static structural consequences ultimately depend on the extent of steel loss, provided the reinforcing bars remain embedded. However, corrosion, especially pitting corrosion, acts as a local stress-raiser, resulting in loss of ductility and reduction in elongation to rupture. Under dynamic or impact loads, the ultimate failure may be brittle.

Although prestressed concrete has generally given excellent performance in the marine environment due to more impermeable concrete and fewer microcracks, when prestressing strands do corrode, the consequences are severe due to the small size of wires (which make-up the strand) and their high state of stress. Such corrosion of prestressing strands as has occurred in marine structures has been in the splash zone, especially where the concrete was highly permeable.

3. Corrosion Rate Versus Component Type/Location

Concrete components located in the intertidal zone and splash zones typically have the highest corrosion rates. Components in these vulnerable locations are constantly subjected to the three primary components which drive the corrosion process: oxygen, chlorides and moisture.

Thus, piles tend to suffer more corrosion than other components because they are located in this zone of highest corrosion potential. However, the portions of piles located below water typically have much lower rates of corrosion because one of the necessary components, oxygen, is in short supply underwater.

Components such as pile caps, beams and decks typically suffer heavier deterioration if they are located in an active marine environment where waves and splash occur, than if they were located in a more benign environment (Ref. 9). For this reason, it is common to see heavier deterioration on the landward (back) components of a marginal wharf structure than the seaward components. As waves impact the slope or retaining wall, chloride-laden spray is directed upwards, ultimately resulting in corrosion of the elements within the spray zone.

The type of concrete construction used can also play a key role in the corrosion process. Flat deck wharves (flat soffit with no pile caps or beams visually evident) typically experience much lower corrosion rates than wharves constructed using the conventional pile/pile cap/beam/deck construction. The reason the flat deck wharves suffer less corrosion is that there are fewer exposed corners. Corrosion occurs more readily on the corners of the components such as pile caps and beams because a) there are two sides for chlorides to penetrate to the reinforcing steel and b) it takes much less pressure to pop-off an exposed corner than it does for non-exposed corners. The typical concrete wharf, with a large deck of reinforced concrete and prestressed piles presents an interesting problem. The deck acts as a large cathode, due to its area in contact with the atmosphere while the piles become the anode.

B. Concrete Deterioration

Deterioration of concrete marine structures may be caused by physical and/or chemical interaction with seawater, resulting in concrete degradation, which may accelerate corrosion of the steel, by loss of protective cover. Concrete deterioration is extremely complex for it depends on parameters that are not always easy to isolate, and which react in varying degrees according to the composition and the exposure of the material. If the structure is fully immersed, the attack on the material by seawater is essentially chemical. In the splash zone, the attack is of chemical and physical nature. The mechanical action of the waves, the swelling and shrinkage caused by the alternate saturation and drying, atmospheric conditions (wind, exposure to the sun, freezing) and the electrochemical corrosion of steel reinforcement are physical processes which add to the chemical

destruction processes" (Ref. 7). Submerged deterioration of the concrete has been limited to what has been identified as secondary ettringite formation, sulfate attack, delayed ettringite formation, alkali-silica reaction and to a lesser extent, by corrosion. Concrete in the splash zone and atmospheric zones is also subject to freeze-thaw attack.

C. Testing Methods for Corrosion Damage

The most common method of testing concrete for corrosion damage is visual inspection and direct measurement. The size of cracks and spalls are measured to estimate the quantities of repair volume that will be necessary for their repair. The remaining diameter of exposed reinforcing steel can be measured directly.

1. Chloride Content Evaluation

In some cases, it may be advantageous to know the concentration of chloride in the concrete at the level of the reinforcing steel. Chloride content evaluation provides an indication of the potential for corrosion of the reinforcing and prestressing steel in the concrete. The presence of chloride in concrete can lead to corrosion of the steel. The chloride may be in water soluble form or may be chemically combined with other ingredients. Soluble chlorides cause corrosion of reinforcing steel, while chloride combined with other ingredients has little effect on corrosion.

While it would appear reasonable to measure the water soluble chloride content only, these tests are time consuming and difficult to control, as there are a number of factors which affect the results (Ref. 9). The test for total chloride, which is the sum of water soluble chlorides and chlorides chemically combined with other ingredients, is not as sensitive to these factors. It has been found that when total chloride content is near the corrosion threshold level, from fifty percent to eighty-five percent of it will usually be water soluble, although in some cases the percentage is lower. Thus, it is recommended that the total chloride content be measured. If the total chloride content is less than the established allowable limit, no further action is necessary. If the total chloride content exceeds this limit, the soluble chloride content should be determined. If this value is also above the limit, corrosion is probably occurring if moisture and oxygen are readily available. If the chloride content is below this value, the risk of corrosion is low. ACI 318 recommends that the following limits be established for water soluble chloride ion in concrete prior to service exposure, expressed as a percent by weight of cement:

- prestressed concrete: 0.06 percent

- non-prestressed concrete: 0.15 percent

These values are established for new concrete, considering that the concrete will absorb additional chlorides during service. Thus, use of these values will yield conservative results.

It is recommended that the procedure described in AASHTO T 260 be followed in determining the chloride ion content of concrete samples. This procedure provides for determining both the total and water soluble chloride ion content. The core which is tested should be drilled at least 75 mm (3 in.) deep. Concrete slices at the 25, 50, 75 mm (1 in., 2 in.,

and 3 in.) depths are then pulverized. The three locations will provide information regarding the variation of the chloride content with depth. The number of locations on the structure which require sampling is a matter of engineering judgement. Since the results of the evaluation do not actually provide a measure of the amount of corrosion, but rather an estimate of the potential for corrosion, it is generally not necessary to perform a large number of tests unless there are significant variations in readings from one portion of the structure or component to another.

2. Half Cell Potential Measurements

Half cell potential measurements may be used to determine whether there is a sufficient potential to generate corrosion of the reinforcing steel. The measurements are taken in-situ and do not require any coring of the concrete. They may be taken subsequent to a chloride ion concentration evaluation, if the results of the evaluation indicate the potential for corrosion (Ref. 11). They may also be taken to supplement the chloride ion concentration evaluation information, or in lieu of it.

The procedure for conducting half cell potential measurements is described in ASTM C 876. In essence, it involves setting up a half cell to measure the electrical potential of the reinforcing steel embedded in the concrete. ASTM C 876 suggests that the readings be taken at approximately 1.22 m (4 ft.) spacings. The results of the tests can be interpreted as follows:

- If potentials over an area are more positive than –200 mv referenced to a copper-copper sulfate electrode (CSE), there is a greater than ninety percent probability that no reinforcing or prestressing steel corrosion is occurring in that area at the time of measurement.

- If potentials over an area are in the range of –200 mv CSE to –350 mv CSE, corrosion activity of the reinforcing or prestressing steel in that area is uncertain.

- If potentials over an area are more negative than –350 mv CSE, there is a greater than ninety percent probability that reinforcing or prestressing steel corrosion is imminent or occurring in the area at the time of measurement.

As described in ASTM C 876, under certain conditions, interpreting the results requires the services of a corrosion engineer or specialist. These include cases where the concrete is saturated with water, where the concrete is carbonated at the depth of the reinforcing steel, and where the steel is coated. In addition, as further indicated in ASTM C 876, half-cell potentials may in part or in whole reflect the chemistry of the electrode environment. Unless this chemistry and the absence or presence of competing electrode reactions is known, a half-cell potential cannot be used to identify the presence of corrosion. The actual rate of corrosion is subject to considerable variation, depending on the resistivity of the concrete.

3. Linear Polarization measurements

Linear polarization measurements are then implemented where half-cell measurements indicate potential corrosion. These give the actual rate of corrosion. It is often found, especially in the atmospheric zone, that even though corrosion has been initiated, rates are very slow.

4. X-Ray Technology

Finally X-ray technology is in the process of development which can reveal corrosion of deeply embedded members such as post-tensioning tendons.

5. Complications due to delamination

Delamination, even without the appearance of rust stain, generally indicates the onset of corrosion. For relatively thin members, i.e. less than 300mm (12 in.) thick and for shallow depths of embedded reinforcement, i.e. 75mm (3 in.) or less, ultrasonic measurements will reveal delamination. A hand-held hammer can also be used as a rapid and low cost method of determining areas for more thorough investigation. A chain-drag can be similarly used on decks. For thicker members, low frequency sonar-acoustic devices are available.

6. Measurement of Current Flux

Measurement of current flux, associated with corrosion reactions, can be used to determine both the location and level of activity. Both surface probes and bulk sensors have been used commercially for corrosion detection and the analysis of cathodic protection field distributions and effectiveness underwater, where localized potential measurements are impossible.

D. Corrosion Protection (State of the Art)

Corrosion of the reinforcing steel is the primary cause of concrete deterioration on the waterfront. Numerous high technology materials and methods have been proposed for new construction and repair to alleviate this problem. Most methods, however, warrant serious consideration of both long term "protection" effectiveness and expense. Alternative materials may introduce different corrosion problems and mechanical properties into standard designs. Coating the reinforcement, which to some proponents, initially seemed to be a simple solution, has evolved into a highly specialized process with many concerns. These range from long term concrete interface adhesion under operational loading, to making it impossible to use proven corrosion mitigation techniques such as cathodic protection. Furthermore, there is no better coating for protecting steel than quality concrete itself. With sufficient cover, concrete has mitigated steel corrosion for more than a century. However, the problem is best addressed by consideration of fundamental corrosion behavior when evaluating high technology schemes, which in most cases necessitate even a greater amount of quality control.

As with other waterfront structures, corrosion is sometimes addressed by consideration of the differences in observed behavior in three zones of environmental exposure. The intertidal zone is the most unique to marine structures and deservedly receives the most attention. Protection schemes for the atmospheric zone are generally similar in nature to those for land bound structures such as bridge decks or parking structures where deicing salts may be used. The submerged zone is frequently ignored due to less degradation than in the other zones. However, significant corrosion has been observed at locations of cracks exceeding a threshold width. Flux measurements have also shown the early development of localized anodic regions that persist even in sound concrete.

1. New construction

• Cover - Pilings with minimal cover (less than 50 mm, 2 in.) have endured the three zones of exposure for decades with no sign of corrosion. This concrete is obviously comprised of quality mix of a previous era without additions for workability or corrosion resistance. In present practice, recommendations recognized internationally (and nationally) for seawater exposure include a cover of at least 50mm (2 in.) in the submerged zone and at least 65mm (2½ in.) in the splash zone. Some ports require 75mm (3 in.) in the splash zone. Tolerances of cover are important and are specified in ACI and other codes and standards. Typically they permit a reduction in cover over the spirals/stirrups of 15mm (0.60 in.).

• Concrete quality, especially impermeability, is widely considered to provide the greatest assurance against corrosion. Both impermeability and diffusivity are considered important, the first to impede capillary penetration by the seawater, the second to minimize penetration of the chloride by ionic exchange. These properties are achieved by low water-cementitious ratios (<.37) made possible by high range water-reducing admixtures and the addition of mineral admixtures such as fly ash and silica fume. Corrosion inhibiting admixtures based on $CaNO_2$ are sometimes included. Available evidence is that they delay the initiation of corrosion and hence prolong useful life.

• Reinforcement materials – Until recently only a limited amount of research has been directed at investigation of alternatives to steel for the manufacture of reinforcement. Although corrosion resistant (in some cases obvious without testing), these alternatives for the most part have been considered too expensive or impractical in view of the changes required in proven designs, to accommodate their different mechanical properties. Recently, however, the unprecedented pursuit of alternatives to the generally accepted fix of epoxy- coated reinforcement has generated consideration of new metals and composites. Both laboratory and limited field results with stainless steel reinforcement, employed for its magnetic properties in deperming piers, has spurred interest in its development for corrosion resistance. Other investigations have been directed at more subtle modifications of microstructure to maintain passivity. But perhaps a more promising approach is to use materials that are not dependent on passivation (or limit chloride contact) such as iron with fine silicate fibers for stifling corrosion. Composite materials offer another approach to circumventing the inherent susceptible nature of steel; however, they introduce a whole new set of considerations, such as moisture adsorption and alkali resistance.

• Barriers – Barriers deserve consideration in new construction whereby direct application to the reinforcement or to the concrete surface they limit environmental contact through inferior concrete or concrete cover. Many of the initial problems of corrosion undercutting and concrete adhesion with epoxy coated reinforcement have been solved with third generation formulations and strict factory quality control. Wrap materials, with associated mastics and fastening systems continue to evolve for covering surfaces including concrete. Any state-of-the-art barrier system should have a means of removal for inspection of the underlying structure. Also, as with reinforcement coatings, they eliminate the possibility of future application of cathodic protection.

- Cathodic protection – This type of protection is being incorporated into new construction, where for a fraction of the cost of subsequent installation, it can be immediately activated or left in a standby mode until needed. Techniques are discussed under existing construction, where its use is particularly effective.

- Electrical isolation of the deck from the reinforcing or prestressing steel in the piling can be obtained by physical separation of the bars at the connection and by use of epoxy coating on the bars or strands protruding from the pile head.

2. Existing construction

- Barriers – The growth of the size and number of patches on individual structures attest to the frequently unsatisfactory nature of spot repairs by epoxy injection, encasement with additional concrete, and the application of surface sealers as these methods are still being practiced today. Improved performance has been obtained where the refurbished reinforcement is coated with zinc silicate. Once corrosion has initiated, the components for corrosion are at the reinforcement surface and barriers can effect little benefit. Structural composite wraps have recently been used where claims are that the requirement for internal reinforcement is eliminated, thereby making corrosion irrelevant. However, the spalling may disrupt the wrap, especially if it is two-dimensional. New penetrating inhibitors have been developed, but their efficacy has yet to be fully demonstrated.

- Cathodic protection – During the past 20 years, various techniques have been employed for the application of current to reinforcement to make it behave cathodically and thereby mitigate corrosion. Simple in theory, success is dependent on reinforcement continuity and proper current distribution. Systems vary primarily in anode configuration for current distribution. In the atmospheric zone, conductive (filled) coatings, imbedded slab anodes, and sprayed sacrificial zinc, are seeing less use, in favor of cementitious overlays over catalyzed titanium mesh. In a few locations, investigations of sprayed "activated" titanium indicate promise. Also, activation mixtures have been developed which reportedly prevent passivation of sprayed zinc. In the intertidal zone, fiberglass jackets, surrounding titanium mesh and filled with concrete, are considered state-of-the-art protection for pilings. Another solution, called the "Lifejacket" includes a zinc mesh anode, with a fiberglass jacket filled with grout (Ref. 4). Another solution, employed infrequently in the submerged zone, is the simple installation of impressed current or sacrificial systems conventionally employed for protection of steel structures. Sacrificial anodes give efficient and economic service where the concrete is saturated.

Steel Structures

A. Typical Corrosion Deterioration

A number of factors influence the rate at which steel corrodes in seawater. Contributing to the corrosion process to varying degrees: water temperature; concentration of oxygen in the seawater; pH value of sea water; marine fouling on piling; salinity of the seawater; velocity of the water flow over the structure; abrasive material in the water; and galvanic effect of unlike

metals. Piling in fresh or salt water can also be subject to loss of area due to chemical attack and abrasion. The corrosion process can further be enhanced by the presence of dissimilar metals with differing electrical potential, which results in current flow and ion transfer. That is, one metal component acts anodically to another, much the same as a sacrificial anode, resulting in loss of steel by ion transfer. In Europe, bacterial corrosion has been reported as "active" in the tidal zone.

The normal profile of corrosion of unprotected steel, as in the case of piling or the supporting legs for offshore oil drilling structures, is shown in Figure 1 based on measurements of the distribution on corrosion of test piling exposed in a partially enclosed basin at Kure Beach, North Carolina. A similar attack distribution was reported by the U.S. Army Engineers based on a survey of steel piling deterioration in several installations along the East Coast of the United States.

"The maximum severity of corrosion in the splash zone just above the high tide level is accounted for by the fact that surfaces in this zone are in continuous contact with highly aerated
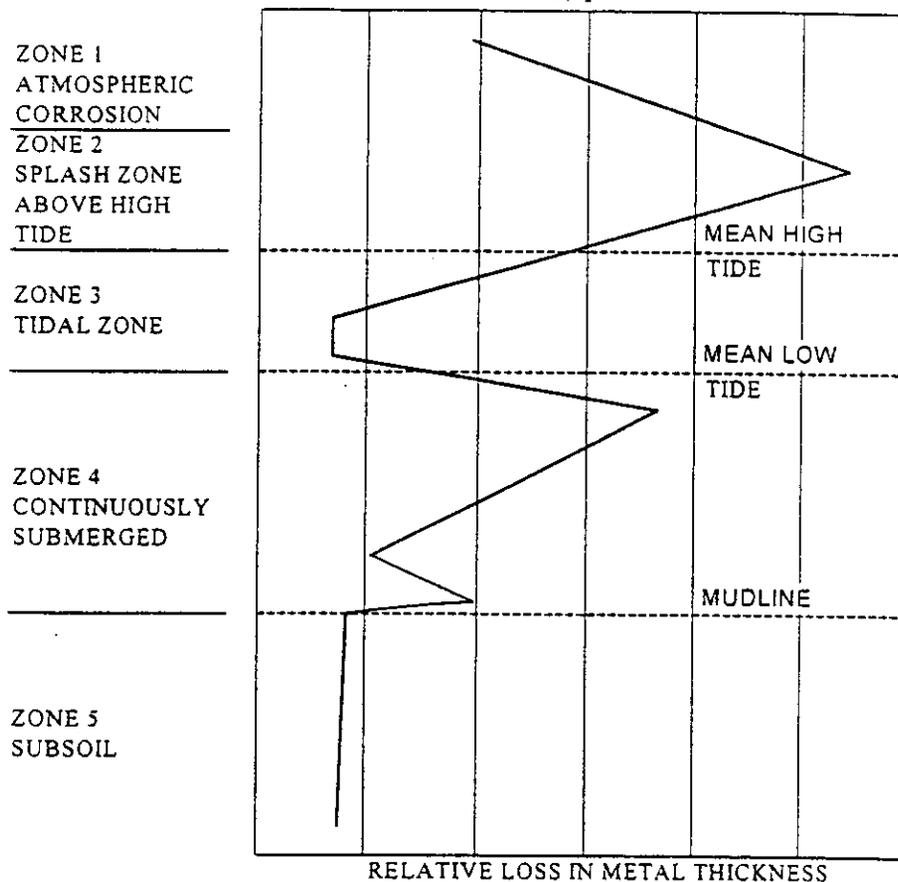

FIGURE 1. CORROSION PROFILE OF STEEL PILING IN SEAWATER

seawater. The minimum corrosion within the tidal zone is due to the differential aeration cell protective effect just described. The secondary peak of corrosion just below low tide is also due to the differential aeration cell action in which the surfaces below low tide become anodic to the tidal zone surfaces. This peak is more evident in shallow water because of the smaller area below low tide" (Ref. 2).

An especially vulnerable zone for accelerated corrosion exists at an interface between bare steel and concrete embedment, for example where steel sheet piles are capped by concrete through the splash zone. Protection by sacrificial anodes is warranted. Corrosion of steel piling is greatly accelerated where moving sands (as in surf zone) or heavy abrasive silt in the current, continuously remove corrosion products as they form, exposing fresh steel surfaces to the corrosion process. Severe corrosion can occur at the mudline where abrasion removes the protective coating of iron oxide, exposing fresh iron, and where there is a strong oxygen gradient. The corrosion rate of steel in seawater is reported to be 3 to 5 mils (.075 to .125mm) per year. This figure is much quoted and can lead to an erroneous conclusion as the rate may vary considerably. Laque (Ref. 5) relates that the corrosion rate at a test site at Kure Beach, North Carolina was a maximum of 0.025 inches per year in the splash zone for each surface.

1. Protective Systems

Corrosion damage in steel structures is the result of a breach in the protective system. Since steel will corrode in the marine environment, a protective system is a requirement for durability. Protective systems generally include one or a combination of the following:

(a) Coating such as galvanizing or special paint systems, such as zinc silicate or zinc-enriched epoxy.

(b) Cathodic protection – active or passive system (below high water level)

(c) Special alloys such as stainless steel, monel, titanium and other alloys may be useful as protective wraps.

(d) Coatings may be compromised by damage, such as scratches or holidays, or by general wear; wraps are especially effective in the splash zone. Coatings typically have a finite lifetime and maintenance must be expected as the structure ages.

(e) Concrete encasement from below low tide line, up into the atmospheric zone.

Cathodic protection systems may fail to protect the structure due to depletion of anodes or by failure of components, as in the case of improper voltage being maintained on an impressed current system. A voltage higher than the system design can in fact accelerate corrosion rates. Intermittent or irregular application of cathodic protection can increase corrosion.

Submerged steel is also subject to galvanic corrosion. Galvanic corrosion occurs when two dissimilar metals are in electrical contact and both are submerged. An electrical current then flows between the two metals causing one of them to corrode rapidly. The speed of the attack is

governed by the composition of the metals, the exposed area, and the electrical conductivity of the liquid. Salt water is an excellent electrical conductor, and galvanic corrosion resulting from dissimilar metals in contact is a significant problem on waterfront structures. The possibility of galvanic corrosion must be considered whenever dissimilar metals are used in marine structures. Welded joints are a local area where corrosion may concentrate. due to dissimilar metallic composition.

An effect similar to galvanic corrosion can occur when there is a difference in environment between different areas on a single metal. When oxygen levels are reduced by limitation in free access of freshly oxygenated water, such as in the threads of a bolt or between structural members, the difference in oxygen content can cause an electrical current to flow between the areas of high and low oxygen content with the result of accelerated corrosion. This effect is particularly severe on some stainless steels and on aluminum alloys. A difference in environment with resulting accelerated corrosion can also be created when a surface is partially covered by an electrically conductive material such as concrete.

Corrosion can also be accelerated by the action of bacteria. In the absence of oxygen. sulfate-reducing bacteria can grow, and the sulfides they produce can cause rapid attack on steel. Barrier systems that are applied without some form of biocide may be susceptible to this form of corrosion. Areas such as the inside of pipe piles that are not filled with concrete can become depleted in oxygen and are frequently the site of sulfate-reducing bacteria attack. Some bottom sediments are oxygen deficient and sulfate-reducing bacterial attack can occur on buried steel in such sediments. Sulfate-reducing bacteria attack is more likely to occur in polluted harbors but can occur whenever oxygen is depleted. The presence of sulfate-reducing bacteria can often be detected by the odor of rotten eggs produced by the bacteria. Sulfate-reducing bacteria attack usually occurs on the inside of pipe piles or below the mudline. It is especially difficult to locate and repair open end pipe piles which are typically not concrete filled. Sulfate-reducing bacteria result in hydrogen sulfide, which is not only deadly poisonous and corrosive but also leads to hydrogen embrittlement of the steel.

Finally, corrosion can be initiated by the presence of stray currents, e.g., from nearby electrical power lines, welding operations or other activities in a shipyard.

2. Structural Consequences

The structural consequences of corrosion of steel structures can generally be correlated with loss of section in the component. The rate of corrosion in unprotected steel can be quite high, depending on the nature of the service environment. This is particularly true in the case of damaged coatings. A holiday in an otherwise intact coating system often results in a concentration of corrosion at the holiday, resulting in aggressive attack and consequent loss of section.

3. Corrosion Rate Versus Component Type/Location

The corrosion process is normally dependent upon three drivers: (a) oxygen, (b) chlorides and (c) moisture. If one or more of these elements is missing, corrosion will generally not occur.

Therefore, it is common for the corrosion rate of submerged steel components to be lower than with components in the splash zone because the oxygen supply is much lower underwater.

Components located in the splash zone often have the highest rates of corrosion. This is due to the high level of available oxygen, the continuous wet-dry process. Cathodic protection systems are less effective in this zone. Coatings may be damaged by floating debris, vessel contact, excessive abrasion or wear.

Steel components that are most vulnerable to corrosion-induced failure are small components such as fasteners, plates and light bracing. This is because a small reduction in cross section represents a larger percentage reduction than it would on a larger component such as a pile or a mooring bollard. Corrosion resistant alloys such as stainless steel, nickel alloys, nickel-copper alloys and titanium may be justified for use where small amounts of corrosion may have significant structural consequences.

B. Testing Methods for Corrosion Damage

1. Ultrasonic Thickness Measurements

It is common practice to use an ultrasonic D-meter to measure the remaining thickness of steel components. Reliable D-meters may be used both above and below water for this purpose. Some units have been designed such that removal of coatings is not necessary; however, the spot chosen for measurement must be free of loose corrosion products and smooth enough to allow uniform contact of the transducer with the steel surface. The results of the ultrasonic thickness testing may be compared to the original design thickness of the member to determine the amount of section loss.

2. Bathycorrometer

Measurement of the voltage on submerged steel components may be used to determine the effectiveness of the cathodic protection system. This may be done using an underwater voltmeter, or bathycorrometer (Ref. 11). Bathycorrometer measurements must be calibrated to the salinity of the water using a conductivity meter. The steel may be regarded as adequately protected if the measured voltage is between −0.83 and −1.1 volts. Voltages of −0.7 and −0.82 indicate partial protection, while voltages less than −0.7 indicate that the steel is cathodically unprotected.

3. Multiple electrodes, positioned at sufficient distance to detect the IR drop associated with electrochemical current fields, are more commonly employed for structures such as submerged (and buried) pipelines, but can also be used for investigation of the corrosion and cathodic protection of pilings.

C. Corrosion protection (State-Of-The-Art)

1. Barriers/coatings

Barriers and coatings are used to protect the steel from corrosion by providing a barrier between the steel and moisture, oxygen and chlorides. The coating type is dependent upon the location and intended use of the steel. Field welded joints can negate factory-applied coatings; these areas must be carefully treated after the welding.

For immersed steel, the steel is in a seawater environment, where the chloride and oxygen contents are relatively low. In this environment a high quality epoxy coating is typically used. Where abrasion resistance is required, glass-flake epoxy coatings are used. For splash zone and underdeck steel, the steel is in an environment where the chloride and oxygen contents are high. In this environment, a high quality epoxy coating is typically used.

For the above deck structural steel, the steel is in an environment where the sodium chloride and oxygen are at moderate levels. In this environment a three-coat system comprised of a primer, intermediate and topcoat are recommended. The primer is typically an epoxy zinc phosphate primer, an epoxy intermediate coat and a polyurethane topcoat. Alternative coatings of zinc silicate are also proving effective.

2. Cathodic protection

Cathodic protection of steel is provided by either passive or active systems. Cathodic protection systems are limited to protection of the submerged portion of the steel. To protect the above water steel and reduce the current demand on the cathodic protection system, coatings are typically applied to the steel.

Passive cathodic protection systems employ sacrificial anodes attached to the steel. The anodes are connected to the steel by bars or cables. Typical sacrificial anode materials are aluminum, magnesium or magnesium alloys. The state of the art for passive systems is the use of galvanic aluminum anodes.

Active cathodic protection systems employ impressed current anodes attached to the steel. The impressed current anode discharges current into a ground, at a rate that causes corrosion of the anode, thereby protecting the steel. The anode materials are selected to corrode at relatively slow rates. Materials used for impressed current anodes are high silicon chrome, graphite carbon, magnetite, platinum-coated titanium, and platinum coated niobium or mixed metal oxide. The most exotic and state-of-the-art anode is the mixed metal oxide anode which maximizes current density, ease of installation and service life.

3. Additional thickness

For many recent major structures, an additional thickness of steel has been provided as "sacrificial steel". This is usually of the order of 10-12mm (0.4 – 0.5 in) of additional thickness.

4. Other

Petrolatum impregnated tapes and mats, fiberglass encased epoxy coatings, concrete and galvanic coatings are also used as barriers or sacrificial coatings. Petrolatum impregnated tapes and mats, and multilayer-coated fabrics provide protective barriers between the corrosive elements and the steel. The petrolatum provides a barrier to the corrosive elements and typically contains corrosion inhibitors. The tapes or multilayer fabric are wrapped around circular, square, rectangular and other shapes where sufficient hoop tension will keep the tape in contact with the steel. The mat material is used for steel 'H' piles and other complex shapes. The mats are held in place by foam shapes that are fitted against the web elements. The foam and mat is then wrapped with a high strength polymer shell.

Fiberglass encased epoxy coatings are also used to provide barriers. The steel elements are encased in fabricated translucent, marine grade fiberglass jacket with a minimum 10 mm (3/8in.) offset. The annular space is filled with a water insensitive epoxy grout. The translucency of the jacket allows the inspector to observe the progression of the epoxy.

Concrete is placed to encase steel within the splash zone. The concrete provides a protective layer around the steel and a relatively dense material that slows the progression of the chlorides to the steel.

Galvanized steel is also used to provide some protection to the steel by providing a sacrificial anodic layer over the steel.

5. Cost-benefit studies

There are many factors which determine the economic as well as the technical life of a marine structure. The additional first cost of measures to prolong the life have to be weighed against the present value of future repairs, and the costs of interruption of service during repairs.

Recently, concerns over safety and protection have become of major importance. The net effect in most cases is the justification of more emphasis on durability, including quality control, and more emphasis on continuing maintenance during the service life.

Barriers to Advanced Methods of Corrosion Control

A. The advanced method of corrosion control must be cost-effective. The owner/operator and the responsible engineer must both be convinced that the solution is cost-effective. In many cases, the facility must remain operational during the rehabilitation.

B. There must be sufficient design information and test data available to the engineer. All requisite design equations need to be provided.

C. The use of coatings on existing structures below the splash zone, have had limited success in the past; development of improved products and application techniques continues in this area.

D F. As cathodic protection of reinforced concrete port facilities becomes more common, installation issues such as "partial" reinforcement continuity, sprayed anode adhesion, and grouting materials for mesh and ribbon anodes should be investigated. Also operational issues such as "effective" potential shift, current distribution, and the effects on high strength strand needs to be addressed.

E G. The issue of galvanic compatibility of stainless steel and carbon steel reinforcing bars in concrete needs to be investigated.

F H. Additives for corrosion control, the focus of earlier investigations, have recently received less attention in favor of reinforcement coatings and consideration of alternative materials for reinforcement. Although still used as "an extra measure of protection", their action is commonly misunderstood. Reputed corrosion "inhibition" or "passivation" in some instances is due primarily to simple inducement of accelerated curing, deterring ion migration in accelerated tests, rather than actual electrochemical process modification. Evaluations of the effects of admixtures used to alter workability, and the usefulness of inhibitors, sometimes accepted in lieu of strict quality control, need to be revisited.

REFERENCES

1. "Eliminating or Minimizing Alkali-Silica Reactivity", Publication SHRP-C-343, Strategic Highway Research Program, Washington, D. C., May 1993.

2. Gerwick, B.C. Jr. "Construction of Prestessed Concrete Structures", 2nd Edition Wiley 1993.

3. Hobbs, D.W., "Alkali-Silica Reaction in Concrete", Thomas Telford Ltd., London, England, 1988.

4. "Kessler, R.J., R. G. Powers and I.R. Lasa, "Zinc Sheet Anodes with Conductive Adhesive for Cathodic Protection", Materials Performance, January 1998, Vol 37, No. 1.

5. Laque, Frances L., "Marine Corrosion" 1975, John Wiley & Sons.

6. Mehta, P. Kumar, "Concrete in the Marine Environment", Elsevier Applied Sciences, 1991 New York.

7. "Performance of Concrete in Marine Environment", Publication SP-65, American Concrete Institute, Detroit, Michigan, 1980.

8. "Petrography Applied to Concrete and Concrete Aggregates", Publication STP 1061, American Society for Testing and Materials, Philadelphia, Pennsylvania, 1990.

9. "Program Manual and Repair Manual, Concrete Wharf Maintenance Program", Port of Los Angeles, Rev. 1999.

10. Romanoff, M., "Corrosion of Steel Pilings in Soils", National Bureau of Standards Monograph 58, October 1962.

11. "Turbid Water Inspection Manual", Korean Ministry of Maritime Affairs and Fisheries, April 1997.

12. "Underwater Facilities Inspection and Assessments of Quaywall and Piers 2, 7,10,11, 12, & 14 at Naval Station, San Diego, California", FPO-1-89 (69) October 1989. Performed for Ocean Engineering and Construction Project Office, Chesapeake-Division, Naval Facilities Engineering Command, Washington, D.C. 20374, by Blaylock-Willis and Associates. San Diego, California 92110.

Workshop Critique

Summary Comments

International Workshop on

Corrosion Control for Marine Structures and Pipelines

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Undoubtedly, the most positive aspect of the Workshop is that it provided a unique opportunity for professionals involved in all facets of corrosion control as this pertains to the spectrum of offshore structures, including both fixed and floating platforms, pipelines, ships, and harbor installations, to assemble, interact, and engage in technical exchange within a dedicated, focused setting. The participants included both management and technical representatives from regulatory bodies, professional societies and trade organizations, major and minor petroleum production companies, the shipbuilding industry, the contractor sector, and academia. On the downside, attendance was impacted by the fact that oil prices had plummeted several months earlier to the ten dollars per barrel range and had not recovered at the time of the Workshop. Participation by practitioners, corrosion control experts, and policy level management from the major oil producing companies was accordingly affected. Although prices have rebounded as of this writing (some six months after the Workshop), the impact of the downturn remains; and planning by the major companies is and will continue to be routinely based upon a worst case scenario. The fallout from this world price structure volatility affects technical aspects of corrosion control as well as all other facets of the industry; and so now, more than in the past, construction, inspection, monitoring, and maintenance strategies must be conceived and accomplished innovatively in order to conform to the economic and personnel limitations that become imposed.

Within the above context, the Keynote, Plenary Session, and Theme Paper speakers did a commendable job of setting the stage for the seven Working Groups. The overriding message of the Working Group Summary Reports reflected a challenging, twofold message. On the one hand, offshore structure technology must maintain an infrastructure that continues to age, not unlike on-shore counterparts but in a much more hostile environment. Inspection methods are inadequate in some instances, particularly in the case of pipelines. On the other hand, the thrust of future petroleum production projects, particularly in the Gulf of Mexico, is toward

progressively deeper waters. Economic viability and competitiveness of such deep water projects dictate, however, that innovative approaches and materials be employed such that over-design, which has been a staple for relatively shallow water structures, is much less of an option. This point was eloquently phrased by one of the Plenary Session presenters, who stated, "Mattie, in deep water you've got to get it right the first time! Every time! No exceptions!" (1). At the same time, the combination of new concepts and innovative, reduced cost materials selection alternatives may be essentially dictated to justify a project. In this regard, Working Group 1 on Subsea Structures and Pipes introduced the concept of risk-based materials selection, a concept that promises to interrelate corrosion control and probabilistic aspects of system integrity. Issues raised by Working Group 3 on Floating Structures presented a special challenge in that these combine standards and procedures of both the shipbuilding and offshore construction industries. Also, floating structures may be deployed for many years prior to a dry dock level overhaul. Working Group 4 on Fixed Structures emphasized that the recently introduced design concept of the Slope Parameter has the potential for rendering cathodic protection more effective and efficient and that this method needs to be integrated into industry standards and recommended practices. Other issues that were emphasized include protocols for cathodic protection retrofits and development of a better understanding of galvanic anode performance. In the case of pipelines, Working Group 5 emphasized a need to better understand both structural and insulating materials, including corrosion resistant alloys, and to develop cathodic protection guidelines for deep water pipes. Also stressed was corrosion modeling of pipe interiors and development of procedures for relating pigging and hydrostatic performance data.

The difficulty of the technical challenge represented by the Working Group recommendations is enhanced by the trend of transiting technical tasks, including design, to contractors who do not necessarily have an incentive or the in-house expertise for innovation, particularly as these pertain to materials selection and corrosion control for new types of systems. This is particularly true in the case of design-build contracts. All too often, corrosion engineering is excluded from the critical path of projects; and personnel with expertise in this field are only able to make after-the-fact, add-on recommendations that are of reduced effectiveness compared to the alternative of early stage involvement and intervention. Offshore petroleum technology is undergoing transitions as never before, and the justification of projects on a life-cycle cost or, alternatively, cost-risk basis is likely to be impacted by design stage corrosion control considerations. The leader of one Working Group emphasized this point in his summary report remarks (2) by pointing out that horses configured radially about a point can only push or pull

against one another; but when arranged linearly and oriented the same, their efforts become complementary and accomplishment is maximized.

References:

1. J. Britton, "Deep Water Corrosion," Plenary Session presentation, International Workshop on Corrosion Control for Marine Structures, February 9-11, 1999, Galveston.

2. W.Revie, "Report from Working Group 5, Pipelines," International Workshop on Corrosion Control for Marine Structures, February 9-11, 1999, Galveston.

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exceed 11 MPa (16,000 psi). [30]. At shallower depths, man can withstand the external pressure if specialized breathing gases are used and long decompression times can be accommodated. For depths in excess of a few hundred meters, man must either provide a pressure barrier between himself and the ocean, or rely on remote presence through robotic craft.

Electrochemistry under deep-water conditions

The possibility of corrosion is determined by the thermodynamics where as the rate of corrosion is controlled by the kinetics. The thermodynamics of corrosion is dictated by the Nernst Equation where the expression for any half-cell reaction may be shown as:

$$e = e^{o} - (RT/nF) \ln K \qquad (1)$$

where the half-cell potential, e, is dependent on the standard half-cell potential, e^{o}, the temperature, T, and the activities of the reacting species and corrosion products that determine the rate constant, K. R and F are the universal gas constant and Faraday's constant, respectively. For any given half-cell reaction, the number of electrons involved, n, also does not change. The standard half-cell potential is a constant for an electrochemical reaction at a given temperature.

NEXT 7 PAGES
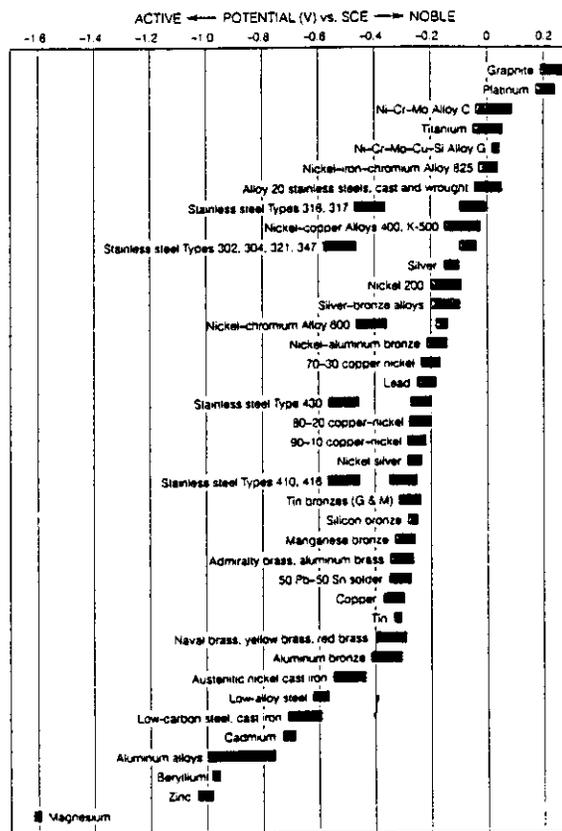
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Figure 6: Galvanic Series for metals and alloys in sea-water.

The basic principle for the establishment of galvanic cells, which is dependent on the presence of dissimilar metals and alloys (different e^o values) in a corrosive environment, is not influenced by the different deep-water conditions of temperature, pressure and ionic activities. Thus, the phenomenon of bi-metallic corrosion will not be any different in deep sea from other atmospheres. Figure 6 shows the galvanic series for common metals and alloys in sea-water. As a thumb-rule, combinations or galvanic couples of metals and alloys, placed widely apart on this chart, ought to be avoided, if possible. The greater the difference in the nobility of the alloys, larger is the driving force for galvanic corrosion.

A close examination of Equation (1) reveals that the half-cell potentials can be altered, i.e. possibility of corrosion can change, if the temperature or the activities of species should change. These factors do change under deep-water conditions. A pressure change influences the activity of gaseous species, such as oxygen and hydrogen, and the enormous volume of solvent affects the ionic concentrations. Every thirty-four feet of water causes the pressure to increase by one atmosphere.

The equilibrium predominance area diagram, known as the Pourbaix's Diagram, determines the potential as a function of solution pH. Regions of immunity, corrosion and passivity can be identified on this diagram. Figure 7 [31] shows the Pourbaix's diagram for iron in water at room temperature of 25°C and various ionic activities of iron, a_{Fe2+}. The concentration of other ions involved in the corrosion reaction will also cause the lines on this diagram to shift.


Figure 7: E vs pH (Pourbaix Diagram) plot for iron in water

Figure 8: Effect of temperature on Pourbaix's Diagram for Fe-H_2O-CO_2 system

It is evident that an increase in the ionic concentration enlarges the zone of passivity. It may be realized that under deep-water conditions, ionic concentrations are expected to be very low due to the enormous solvent volume. Such a decrease in ionic concentration will cause the region of passivity to shrink, or in other words, the regions of corrosion to expand. This aspect may be visualized in another way. High ionic concentration will cause the solubility limit of the solute ions to be reached faster. Thus, further generation of metal ions can be impeded causing an enlarged passivity region.

The role of temperature is evident in Figure 8 [32], which shows the Pourbaix's diagram for the $Fe-H_2O-CO_2$ system. An increase in temperature of $25°$ shows the partial collapse of the passive region. By the same token, a decrease in temperature in deep-water should expand the region of passivity or decrease the areas where corrosion is supported. It is cautioned that these diagrams are equilibrium diagrams, and as such, assumes the achievement of equilibrium.

The effect of gas pressure influences the possible cathodic reactions in deep-water. Figure 9 shows the stability of water as a function of pH. At active potentials water is dissociated into hydrogen gas where as, oxygen is generated at relatively noble potentials at any given pH value.

The influence of hydrostatic pressure can be examined for the reactions where hydrogen or oxygen is involved by the following cathodic reactions:

$$2H^+ + 2\,e^- \rightarrow H_2 \tag{2}$$
$$2H_2O + O_2 + 4\,e^- \rightarrow 4OH^- \tag{3}$$
$$2H_2O + 2\,e^- \rightarrow 2OH^- + H_2 \tag{4}$$

Figure 9: Effect of pressure on the stability of water shown on E vs pH plot

potentials and unfavorable relative areas of anode and cathode. Pin-holes and holidays in the coatings negatively influence the relative areas, causing the active metals to corrode faster. Inert metallic coatings are, therefore, ineffective. Zinc or aluminum active metal coating is useful to protect steel galvanically. If these metals are used to protect the structural alloys beneath a non-metallic coating at coating defects, cathodic protection is effective and inexpensive.

Prominent non-metallic coatings are **Anti-fouling coatings**, that prevent settlement of fouling spores and organisms by continuous release of toxic substances, and **Self-polishing copolymers** [SPC], that incorporate toxins in matrix which are sparingly soluble in sea-water. Thus, fresh paint/water interface is continuously generated. It should be emphasized that in these systems some form of erosion is required for sufficient dissolution of toxins. Additionally, **silicone-rubber-based** materials are also used as coatings, such as, polydimethylsiloxanes. Typical toxins used for deep-water protection are cuprous oxide and tributyl tin oxide. Fouling is prevented by a release of $10\mu g/cm^2/day$ of toxins. For deep ocean structures, a 0.012-0.015 in. organic barrier coating is used [34].

Stainless steel has excellent corrosion resistance in deep-sea environment. Cladding of less expensive metals and alloys by stainless steel is viable option. However, there is a cut-off where cladding is less effective than application of a paint (Figure 10). Additional protection of concrete structures is realized by **encasement** of concrete using bitumastic coatings, bagged and sacked concrete, metallic sheathing, epoxy resins and gunite.


Figure 10: Comparison of stainless cladding and paint repair as a function of life.

Hydrogen embrittlement

High strength welded structures are particularly susceptible to hydrogen damage. Table I shows the amount of total hydrogen present in a medium-carbon high-strength steel. It should be noted that it is only the diffusible hydrogen that is damaging to the steel. There are several sources of hydrogen in deep-sea environment. Use of cathodic polarization to prevent corrosion of steel in underwater service influences the hydrogen ion discharge on the metal surface. However, the sensitivity of a particular steel to embrittlement is dependent on amount of hydrogen entering the steel and the operative stress system. Hydrogen damage is dependent on the loading condition, where a static tensile load is typically required for hydrogen cracking of steel. Depending on the structure, the hydrostatic pressure could load the structure in tension, compression or both. Embrittlement is not caused under protective potentials of around -0.8 V vs. SCE. However, the role of over-protection, high hardness regions and sulfate reducing bacterial interaction by anaerobic growth (SRB) could give rise to embrittlement. The role of microbial reactions on generation of hydrogen sulfide is shown in Figure 11 [35].

Table I: Total hydrogen content of steel under different corrosion conditions

| Environment	Sample type	Exposure time (h)	Total hydrogen level (ml/100 g)
(Air)	BS 4360 : 50 D	0	0.06
	Weld metal	0	0.05
Sea-water with cathodic protection by Zn at +20 °C	Weld metal	1000	0.05
		4000	0.05-0.08
Sea-water with 100 p.p.m. H_2S	Weld metal	350	0.08
		2500	0.02-0.2
NACE	BS 4360 : 50 D	100	8.3
		525	7.8
	Weld metal	100	1.1-2.7
		525	0.5-3.0
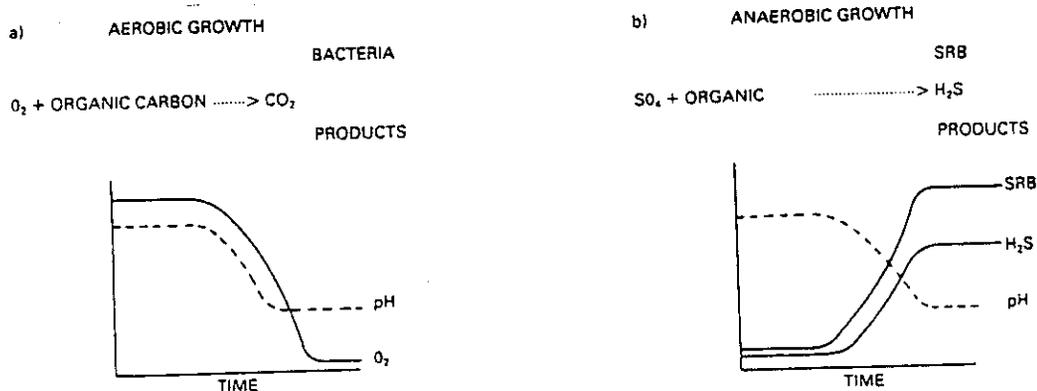
Figure 11: Generation of H_2S gas by anaerobic bacterial growth

Figure 1, General process of using smart pig data on reliability estimation

Remaining strength of pipelines based on data collected by smart pigs

In the last two decades metal loss measured by smart pigs are employed in estimating the remaining strength of corroded pipelines, by applying the criteria indicate in ASME B31G Manual for Determining the Remaining Strength of Corroded Pipelines, which is based on a semi-empirical fracture mechanics relationship originally develop by Folias (1967), to simplify the evaluation of a corroded pipeline, the area of metal loss A is usually represented by a parabola as shown in figure 2.

Figure 2, Longitudinal view of a corroded pipeline

So the calculation of A on the basis of two parameters of the metal loss; its length (L) and maximum depth (d), this give A= (2/3)Ld and the non corroded area Ao= Lt, using this and the flow stress equal to 1.1 SMYS, leads to the hoop stress at failure by the following formula:

$$\sigma = 1.1 \, SMYS \left[\frac{1 - (2/3)(d/t)}{1 - (2/3)(d/t)(M^{-1})} \right]$$

Where:

S	Hoop stress at failure
SMYS	Specified Minimum Yield Stress
D	Maximum corroded depth
T	Nominal wall thickness
M	Folias factor

However this criteria has a excessive conservatism mainly due to:

- Expression for flow stress
- Approximation used for Folias factor
- Parabolic representation of metal loss
- Variability of corrosion depth along pipe axis